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Abstract

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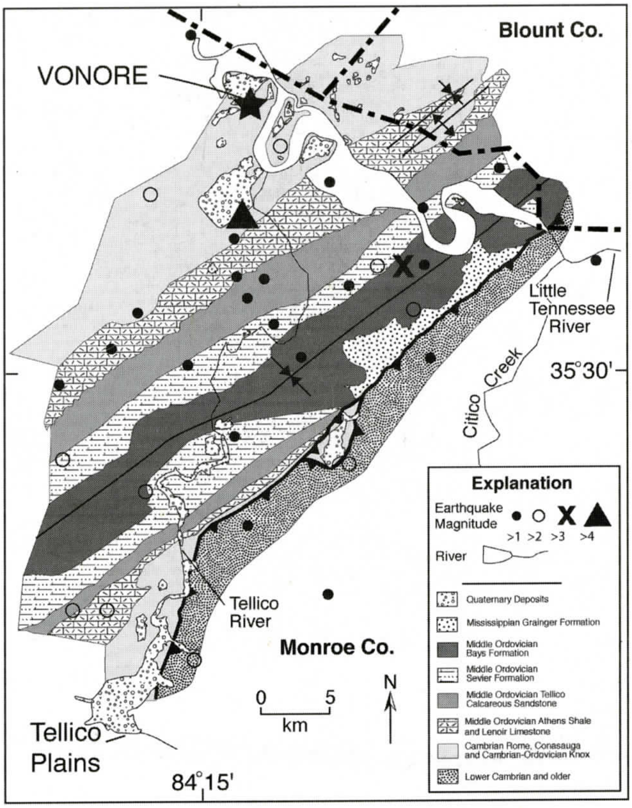

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DISTURBED SEDIMENTS IN THE EAST TENNESSEE SEISMIC ZONE: EVIDENCE OF LARGE PREHISTORIC EARTHQUAKES IN EAST TENNESSEE?

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ABSTRACT

Earthquakes occur in the East Tennessee seismic zone with greater frequency than anywhere east of the Rocky Mountains outside of the New Madrid seismic zone and the Charlevoix region in Canada. No earthquakes greater than M = 4.9 have been recorded in the East Tennessee seismic zone, although the observation window of historical seismic activity is narrow. It is possible that large earthquakes have occurred in the past, but the absence of large historical earthquakes has discouraged study of this seismic zone. The concentration of critical infrastructure and large population centers without knowledge of the earthquake history of this area is potentially dangerous. Two localities where anomalously deformed sediments occur have recently been discovered in the East Tennessee seismic zone. An outcrop of disturbed and folded sediments in Tellico Plains, Tennessee, and filled fractures and faults in a Miocene lake deposit near Gray, Tennessee, could be the result of seismic activity. These features, combined with the level and extent of instrumentally detected seismicity, emphasize the need for continued study to properly assess the seismic hazard of this zone.

INTRODUCTION

Seismic hazard assessment is ideally based on estimated recurrence intervals of earthquakes with moment magnitudes **M**>5.0 (Bollinger and others, 1993; Frankel and others, 2002). Large earthquakes (**M** ≥ 6.5) are frequent along faults at the active plate boundary in the western United States. Shorter recurrence intervals of large earthquakes place better spatial and temporal limits on these assessments. Despite being considered a stable intracratonic region (Johnston and others, 1994), large prehistoric damaging earthquakes, like the 1811-1812 New Madrid sequence, have occurred in the eastern United States (Russ, 1979; Zoback and others, 1980; Russ and others, 1981; Johnston and Nava, 1985; Talwani and Cox, 1985; Van Arsdale, 1986; Obermeier, 1989; Zoback, 1992; Schweig and Van Arsdale, 1996; and Tuttle and others, 1996). Because of the long recurrence intervals of large earthquakes, hazard assessment in this region is more difficult and based almost entirely on single large historical events or event clusters and statistical assessment, not on modern seismicity. The 1727 and 1755 Cape Ann, Massachusetts, the 1811-1812 New Madrid, and the 1886 Charleston earthquakes are the best-documented large historical events in the eastern United States and these areas are considered high hazard primarily due to relatively short repeat times for large events (Ebel, 1984; Frankel and others,

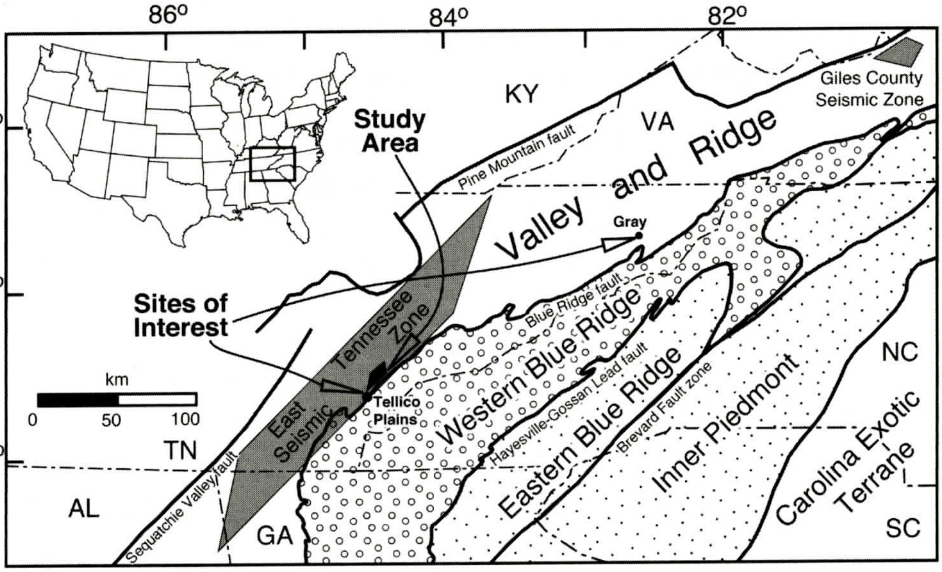


Figure 1. Simplified tectonic map of the southern Appalachians showing the location of the Valley and Ridge, the sites studied, and the Giles County and East Tennessee seismic zones. Modified from Hatcher and others (1990).

2002). Conversely, seismic hazard determinations for regions without documented, large historic or pre-historic earthquakes (e.g., the East Tennessee seismic zone) are typically much lower even when small earthquakes are common within these regions.

While the maximum magnitudes of large earthquakes in the eastern and western U.S. are similar, the areal extent of damage is likely to be very different. Lesser attenuation by the more intact eastern United States crust has meant that large earthquake damage extends over a region approximately twice as large as that affected by comparable earthquakes in the western United States (Bollinger and others, 1993). For instance, the Cape Ann earthquakes (estimated **M** = 6.1) damaged Boston and eastern Massachusetts and were felt by ships at sea 300 km away (Stover and Coffman, 1993). The Charleston earthquake (estimated **M** = 7.3) (Johnston and Schweig, 1996; Talwani and Schaeffer, 2001) affected most of the United States east of the Mississippi. Four of the New Madrid events that occurred in 1811-1812 produced an estimated magnitude of at least **M** = 8.1 (Johnston and Schweig, 1996); they were felt over most of the eastern United States. Physical evidence of Charleston and New Madrid events includes soft-sediment deformation, sand geysers and dikes, small fault scarps, and damaged man-made structures. These areas have therefore been studied intensely to determine the future risk of large earthquakes. The New Madrid region is unlike Charleston and Cape Ann because it continues to produce many small magnitude earthquakes (Bollinger and others, 1991). Although it lacks a large documented earthquake, the East Tennessee seismic zone (ETSZ) is otherwise very similar to the New Madrid seismic zone in terms of modern seismic activity. This study was conducted to determine if there is evidence of large Holocene earthquakes to better assess the seismic hazard of eastern Tennessee in light of the region's concentration of seismicity.

EAST TENNESSEE SEISMIC ZONE

Earthquakes occur frequently within the ETSZ (Moneymaker, 1954, 1955, 1957, 1958; Bollinger, 1973; Bollinger and others, 1976; Chapman and others, 1997) (Figure 1). It pro-

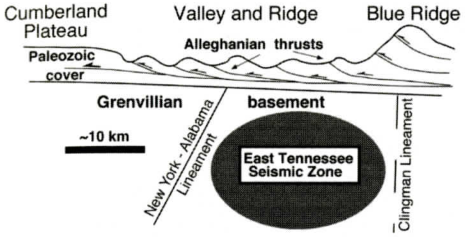


Figure 2. Schematic cross section of the crust in and near the ETSZ showing average depth of earthquakes, locations of geophysical lineaments, and thickness of Paleozoic cover.

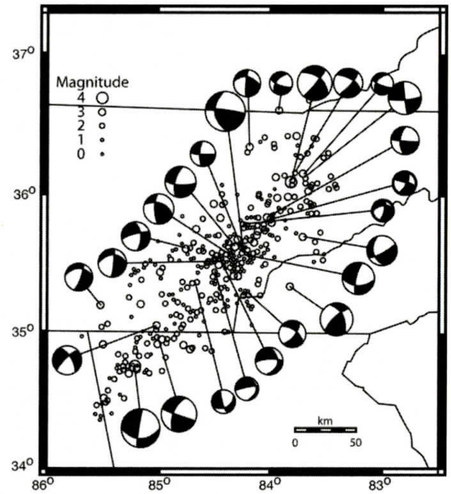


Figure 3. Lower hemisphere equal-area projections of first motions of earthquakes in the ETSZ. Most of the faults have strike-slip motion with very little vertical component. (From Chapman and others, 1997.)

duces more earthquakes per year than any seismic zone east of the Rockies except for the New Madrid seismic zone and Charlevoix region in eastern Canada. Most earthquakes in the ETSZ are generated at depths of 8 to 25 km (Chapman and others, 1997) and are thus located in crystalline basement below the thin-skinned Valley and Ridge foreland fold-thrust belt (Figure 2). The 1897 earthquake in the Giles County seismic zone (GCSZ) in Southwest Virginia (estimated M = 5.8), the largest earthquake recorded in the southern Appalachian Valley and Ridge, may have caused surface faulting and folding (Callis, 1996; Law and others, 2000). Although earthquake density is higher in the GCSZ, the GCSZ has a lower overall rate of earthquake occurrence, and is separated from the ETSZ by a region of low earthquake activity. The two largest earthquakes in the ETSZ, the April, 2003 M_{BLg} 4.9 earthquake in Mentone, Alabama, (now the largest earthquake recorded in this zone) and the 1973 M_S 4.6 earthquake that occurred near Maryville, Tennessee, damaged nearby chimneys, walls, and windows (Stover and Coffman, 1993). Earthquakes of this size are not large enough to cause more than very localized surface deformation and damage, and the largest recorded earthquakes in the ETSZ are below the accepted M~5 threshold for surface rupture/displacement (McCalpin, 1996).

First-motion studies of many instrumentally recorded earthquakes in the ETSZ indicate primarily north-south or east-west strike-slip motion (Figure 3; Chapman and others, 1997). Seismologists have modeled the focal mechanisms (Teague and others, 1986; Chapman and others, 1997), created seismotectonic models (Powell and others, 1994; Kaufman and Long, 1996) to better understand the seismicity, and measured the stress field in the area (Zoback, 1992). Powell and others (1994) examined records from 1698-1977 and concluded the earthquake zone may have moved during the almost three centuries from the North Carolina-Tennessee border region to wholly within Tennessee. Given the decreased accuracy of historically recorded earthquakes versus the instrumentally located earthquakes, this apparent movement of the locus of earthquakes may reflect human population movement as much as movement of seismicity over such a short geologic time span.

According to the seismotectonic models, the earthquakes are concentrated between the prominent New York-Alabama magnetic and gravity lineament (King and Zietz, 1978) to the west and the weaker Clingman magnetic lineament (Nelson and Zietz, 1983) to the east. These anomalies are thought to represent boundaries between two different types of Grenville crust (Nelson and Zietz, 1983; Hatcher and others, 1987). The ETSZ is in a low seismic velocity crustal zone (6-6.2 km/s) flanked

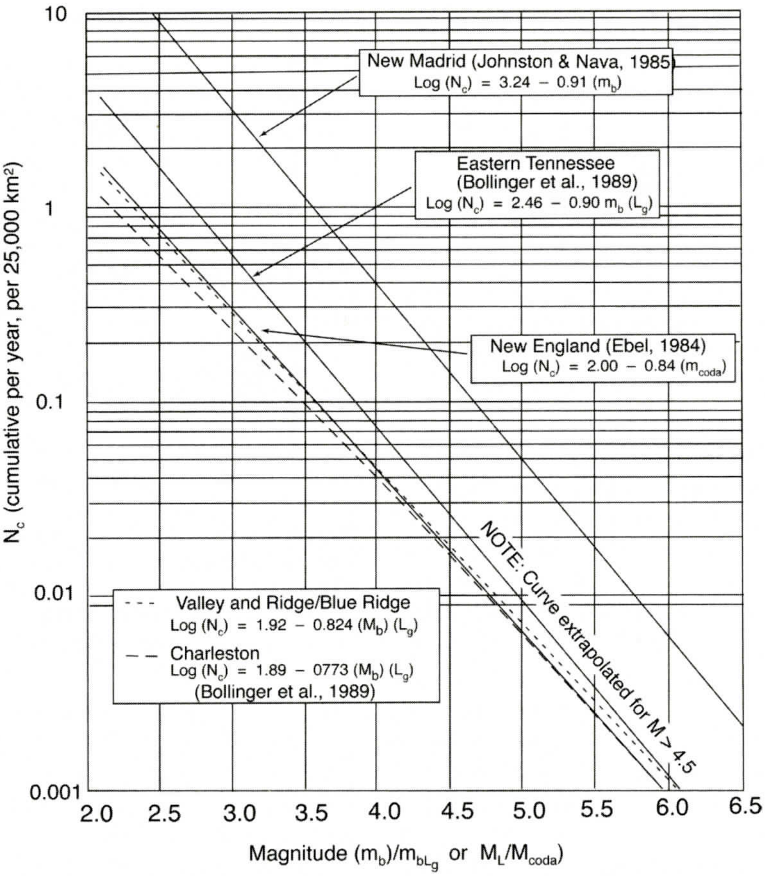


Figure 4. Curves showing magnitude of earthquakes against earthquakes per year per 25,000 km² plotted for seismic zones in the eastern United States.

on either side by higher velocity zones (>6.3 km/s) (Kaufman and Long, 1996; Vlahovic and others, 1998). Hatcher and others (1987) suggested the New York-Alabama lineament is a seismic barrier that limits elastic strain accumulation and controls maximum earthquake size. Kaufman and Long (1996) hypothesized that the low velocity zone is a highly fractured and fluid-filled region in the crust. Faulting in Grenville basement rocks has been identified (Woodward and Gray, 1985; Mitra, 1988; Costain and others; 1989, Hatcher and others, 1994) and recently collected industry seismic lines in northeastern Tennessee show basement faulting passively affecting overlying Paleozoic structures (Tavernier, 2002), although the faults probably have not been active since the Eocambrian, perhaps due to their 042 orientation.

Given the modern seismic activity of the ETSZ and its similarity to the New Madrid zone in geophysical signature, areal extent, and shape (Powell and others, 1994), the current study was designed to determine if there have been damaging earthquakes in this region. Earthquakes have been reported in this area as early as 1776 (Moneymaker, 1954; Reinbold and Johnston, 1987), but none are known to have been large enough to cause geologically recorded disturbance. Given that large earthquakes in the ETSZ may have recurrence intervals of centuries, the lack of large historical earthquakes is likely related to the comparatively short historical record (Figure 4). Considering that historical records here cover only the past 225 years and the heavy vegetation in this region, a large prehistoric earthquake may have occurred here and not been detected. Earlier studies looking for evidence in this area have been reconnaissance (Cato and others, 1992) or anecdotal and related to other work (Delcourt, 1980).

POTENTIAL EARTHQUAKE EVIDENCE

Evidence of past large earthquakes is divided here into two categories: primary and secondary. Fault scarps and other surface ruptures are examples of primary features that could be caused by earthquakes. Secondary features include drainage basin changes, landslides, and liquefaction features. All of these may occur in East Tennessee, but the humid climate with its rapid weathering and erosion, dense vegetation, topographically varied terrain, and human disturbance make them challenging to find (Ahnert, 1970; Crone and others, 1992; Machette and others, 1993). The most obvious geologic evidence of a recent earthquake is a fault scarp. This should produce a low ridge representing displacement between upthrown and downdropped blocks of crust. Ideal strike-slip motion would produce little vertical offset, but pure strike slip motion is rare. Fault scarps would most likely be found through a combination of aerial photo analysis, drainage analysis, and field work. Distinguishing a small recent scarp in the 100 m or more of common relief in the East Tennessee Valley and Ridge is difficult unless the scarp can be observed in a flood plain or stream terrace, or cuts a prominent marker. Because most earthquake foci are located deep in the Grenville basement and because first motion studies indicate predominantly strike-slip faulting, formation and survival of fault scarps in Appalachian Valley and Ridge bedrock and younger cover may be unlikely. Drainage pattern analysis (Merritts and Hesterberg, 1994) may be helpful in finding surface deformation in a coastal plain, but is not applicable here because of strong bedrock control of drainage, particularly the northeast strike of Paleozoic units and prominent joint sets in the Valley and Ridge (Hatcher and others, 1992).

Earthquakes also trigger landslides (Jibson, 1996). Given the right conditions (dip of bedding, cleavage, or prominent fracture set parallel to the slope; weak material; water saturation; and steep slopes), even low magnitude earthquakes (M_b >4) can trigger landslides (Keefer, 1984). Occurrence of landslides, however, is not sufficient evidence of earthquakes. Landslides must be evaluated to determine if the mass movement could have been triggered by other means such as heavy rainfall or natural undercutting of slopes (Jibson and Keefer, 1993; Hatcher and others, 1996). This permits use of landslides as supporting evidence when independent proof of an earthquake trigger is found. Dating of material entrained in landslide deposits has provided links to earthquakes known independently from other geologic, paleoseismic, or historical evidence (Jacoby and others, 1992; Jibson, 1996).

Definitive evidence of large ETSZ earthquakes may ultimately come from liquefaction features. Liquefaction occurs where unconsolidated, water-saturated sediment is shaken during an earthquake, loses cohesion due to increased pore water pressure and dewatering, and undergoes spontaneous viscous flow. If an overlying impermeable layer is hydraulically fractured by this moving liquefied sediment, the sediment will propagate fractures until it no longer has the pressure to fracture the layer, forming sand dikes and sills (McCalpin, 1996). Removal of material beneath the impermeable layer may cause the layer to collapse, forming a crater, or move and fracture overlying sediments horizontally into discrete blocks by lateral spreading. If a sand dike reaches the surface, it may have enough pressure to form a sand geyser, also called a sand blow or sand boil. These features are all well documented where major earthquakes have occurred in unconsolidated sediment at Charleston, South Carolina (Obermeier and others, 1985; Talwani and Cox, 1985), New Madrid seismic zone (Russ, 1979; Obermeier, 1989; Tuttle and Schweig, 1995; Tuttle and others, 1996), Wabash Valley, Illinois (Obermeier and others, 1985; Obermeier, 1998), and along the Pacific Coast of Washington (Obermeier, 1994). Many of these features are readily observed in aerial photographs of

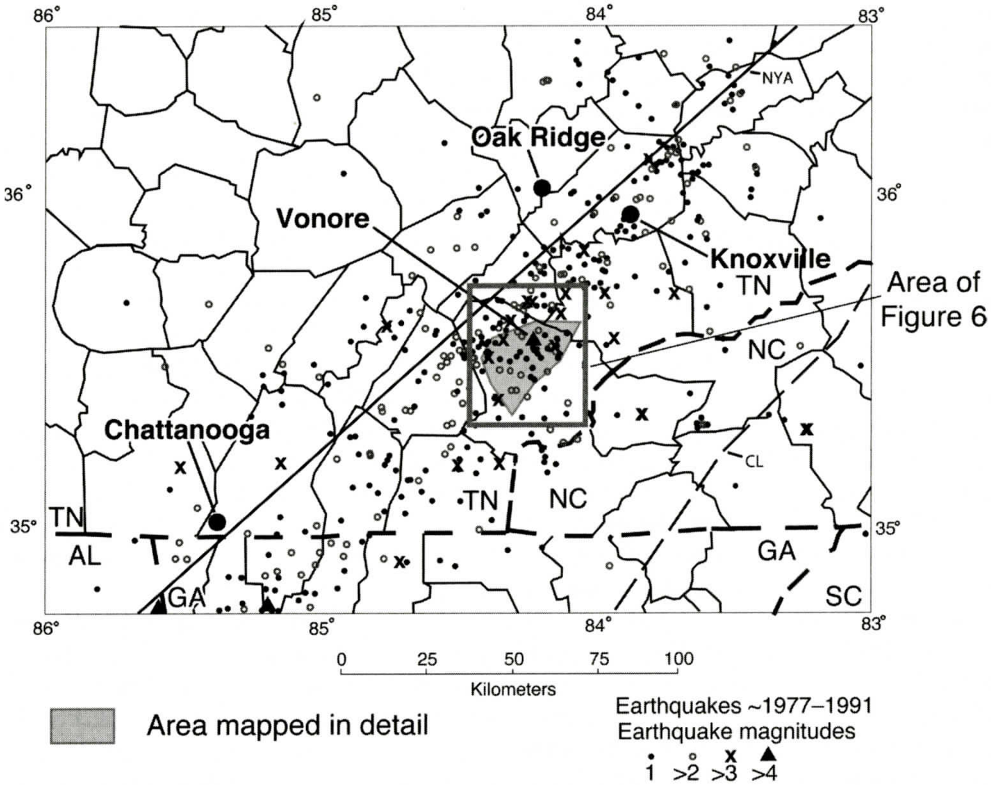


Figure 5. Earthquakes in the ETSZ 1977-1991 also indicating the location of the April, 2003 M=4.9 earthquake near Mentone, Alabama. Earthquakes are concentrated between the New York-Alabama lineament (solid) and weaker Clingman geophysical lineament (dashed). The greatest concentration of modern earthquakes occurs near Vonore, Tennessee.

major river flood plains, even where they are not visible at ground level. Liquefaction features are difficult to create aseismically, thus providing convincing evidence of earthquakes (McCalpin, 1996). Folded sediments and load structures may also be created by cyclic shaking by an earthquake, but can be formed by other geologic processes (Obermeier, 1996).

LOCATION OF STUDY

The location of the greatest concentration of modern earthquakes in the ETSZ is near Vonore, Tennessee (Figure 5). One of the largest modern earthquakes in the ETSZ (M=4.2) occurred in Vonore in 1987. Detailed geologic mapping of bedrock and surficial materials was conducted in this area because of this high concentration. The Vonore, Tennessee, area is drained by the Little Tennessee and the Tellico Rivers. Both have well–developed flood plains; the Little Tennessee, the larger of the two, has a large flood plain that has unfortunately been largely inundated by a TVA reservoir. Extensive archeological work was performed on the flood plain of the Little Tennessee before it was dammed. The reports did not identify features such as sand dikes or offset beds that could be related to seismic activity (Chapman 1977, 1980), but one possible offset was observed in a prehistoric Native American stockade wall (Delcourt, 1980). The Tellico River is a tributary of the Little Tennessee, and a significant portion of its flood plain remains exposed. Both rivers have less exposed and less extensive older terraces. Although the Vonore area was considered the most likely place to find evidence of large earthquakes, other possibilities outside the

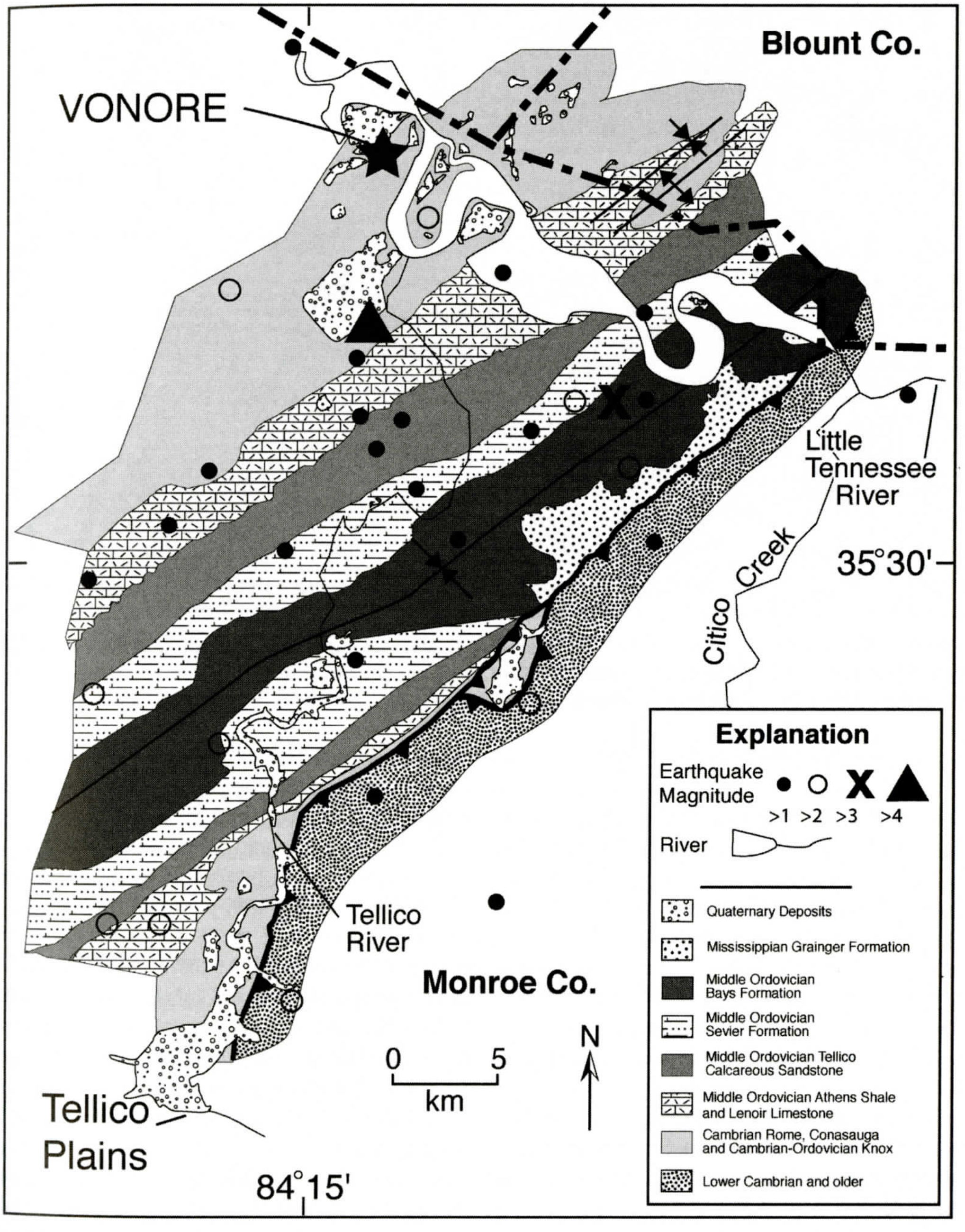


Figure 6. Detailed geologic map of the most active area in the ETSZ showing rivers and location of Tellico Plains (TP) disturbed terrace deposit. Teeth are on hanging walls of faults. The town of Vonore is marked with a star.

immediate area were investigated. Landslides, precariously balanced rocks, soft-sediment deformation, fractures in soft sediment, liquefaction features, and other evidence that would suggest a prehistoric large (M>6) earthquake were all considered as viable targets for investigation.

Figure 7. Aerial photograph of Gray site showing Quaternary alluvium-cap over darker organic layer. Clastic-filled fault is highlighted to left of deposit. (Photograph courtesy of Harry Moore, Tennessee Department of Transportation.)

GEOLOGIC MAPPING

Detailed 1:24,000 scale geologic mapping of bedrock and surficial materials was carried out to better distinguish Alleghanian structures from those possibly related to large recent earthquakes. A geologic map was produced of the area between the Little Tennessee and Tellico Rivers (Figure 6) by collecting data from foot, road, and canoe traverses along these rivers and between the Great Smoky fault (to the SE) and U.S. 411 (to the NW).

Traverses focused on locating through going recent faults or liquefaction features in riverbanks that are not visible using other data sets such as aerial photography. Work along the Little Tennessee River also focused on the higher terrace deposits, which are more common there than along the Tellico River.

Flood plains and old river terraces are the most likely locations for finding geomorphological evidence of a major paleoseismic event. Studies of the New Madrid seismic zone focused preliminary searches along the banks of drainage ditches because of the increased likelihood of finding paleoseismic evidence in the ditch banks (Johnston and Nava, 1985; Van Arsdale, 1986; Tuttle and others, 1996). Terrace deposits have also been studied (Chapman, 1980; H.H. Mills, 1999, personal comm.), but the planar nature of these deposits and their proximity to water make them good farmland and consequently they are substantially altered. Tellico Reservoir, which now covers much of the flood plain and some of the lower terraces of the Little Tennessee River, is kept at an elevation of about 248 m (813 ft) during the summer months; during the winter, the reservoir is lowered 3 m (10 feet) exposing a small portion of the flood plain. Prereservoir soil surveys, aerial photographs, and topographic maps have been analyzed to determine probable locations for suspect sand blows and dikes near the current shoreline. No obvious sand blows or dikes were found using these techniques.

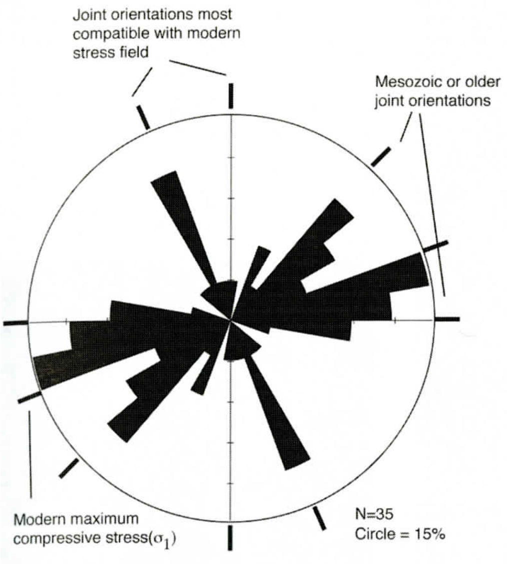


Figure 8. Rose diagram indicates fractures within the Cenozoic deposits at the Gray site are generally aligned with fractures in the underlying bedrock.

Other Study Areas

Two other sites have been studied and warrant more thorough investigation. The Gray fossil site in northeastern Tennessee has possible liquefaction features (clastic-filled dikes), and a site in Tellico Plains, Tennessee, had deformed deposits.

Gray Fossil Site

The Gray fossil site, discovered in the summer of 2000, is not within the modern boundaries of the ETSZ defined by Powell and others (1994). This site contains one of the few well-preserved Miocene mammalian fossil assemblages in the U.S. and only the second of Miocene age of any size (Whisner and others, 2001). This location, near Gray in NE Tennessee, (Figure 1), is the site of a Miocene lacustrine deposit of organic fossil-rich clays and alluvium resting on Cambro-Ordovician Knox Group. The organic-rich black and gray Miocene clays are capped by orange cherty, sandy, clayey Quaternary alluvium (Figure 7). Joints and fractures with little offset exist throughout the clay. These fractures predominantly trend east-west, northeast-southwest, or south-southeast (Figure 8), orientations consistent with underlying bedrock orientations for Mesozoic and modern stress fields (maximum compressive stress 070) (Hatcher and others, 1992; Zoback, 1992). The existence of these fractures suggests possible inheritance from underlying bedrock, indicating movement since deposition, or they may be products of the late Tertiary to Holocene stress field (Engelder, 1982).

This site contains apparent dewatering features in the clay deposit (Figure 9). The primary expression of dewatering is a clay- and gravel-filled fracture on the south side of the site. Occasional sand and gravel lenses exist throughout the deposit, one of which may have been cut, dewatered, and provided fill for the fracture during earthquake shaking or alternately sinkhole collapse (Figs. 9a and 9b). This fracture apparently propagated up-section from or through a layer of highly organic, less permeable clay into a cap layer of less organic, lighter-colored clay. It is not clear if it extended into the overlying alluvial layer. Although the fracture has an aperture of only a few cm, it is traceable up section for 5 to 10 m. This feature, while intriguing, was not studied in detail. More of these filled fractures exist, but the site has been covered with grass and is currently being preserved as a paleontological repository of Miocene fauna and flora, and trenching the fractures is presently not feasible.

Tellico Plains

In early October, 1999, a deformed deposit along the Tellico River was observed along a Tennessee Department of Transportation (TDOT) excavation widening Tennessee Highway 165 through Tellico Plains, Tennessee (Figure 1). This deposit overlies Cambrian Sandsuck Formation siltstone in the hanging wall of the Great Smoky fault, and the extent of weathering (deep weathering rinds in cobbles) indicates at least an early Holocene or late Pleistocene age, although the absolute age is unknown.

After initial investigation, a trench was cut perpendicular to the face of the 3 m vertical exposure. Because this locality was scheduled for

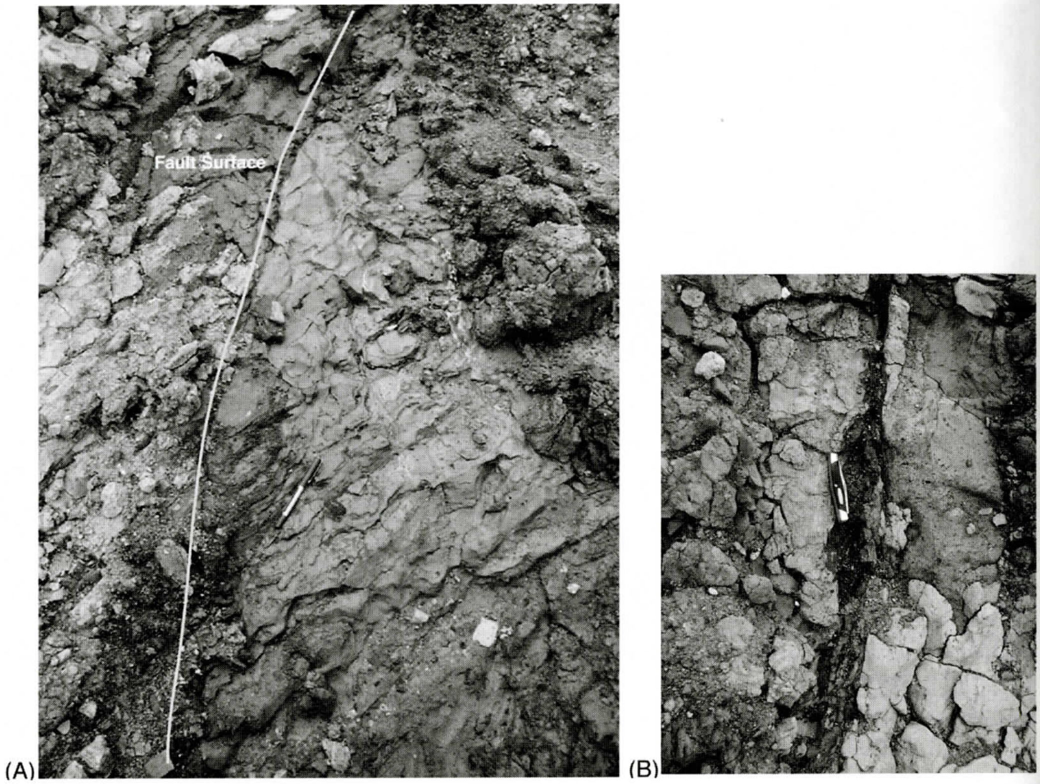


Figure 9. a. Fault in Miocene Gray deposit clay looking south on a gently sloping surface. To the right is the upthrown block. Offset is a few meters. Line traces fault surface. b. Close-up of fault. Fill material is dark clay and pebbles. Knife is 7cm long.

destruction during widening of the highway, trenching and investigation of the exposure were done during a short period of time before removal of the entire exposure by TDOT in November, 1999. Only one trench was excavated, and this trench yielded few data because the de-

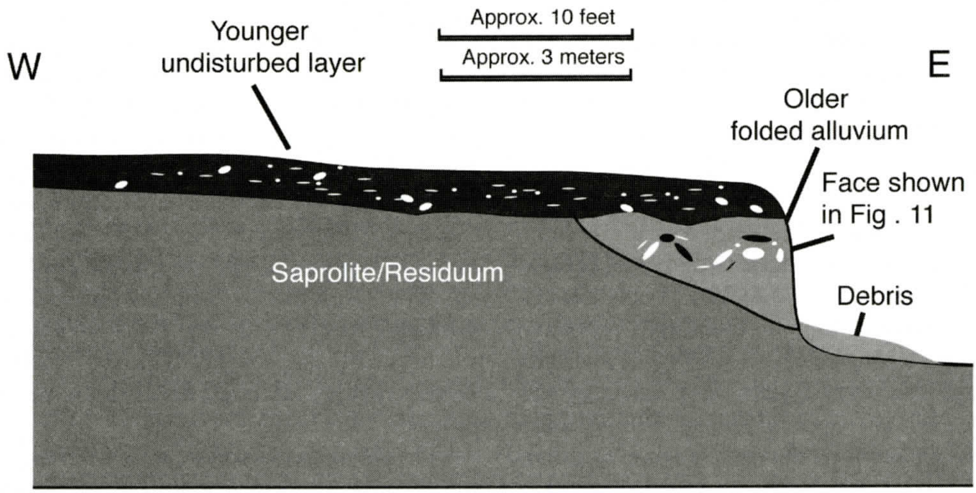
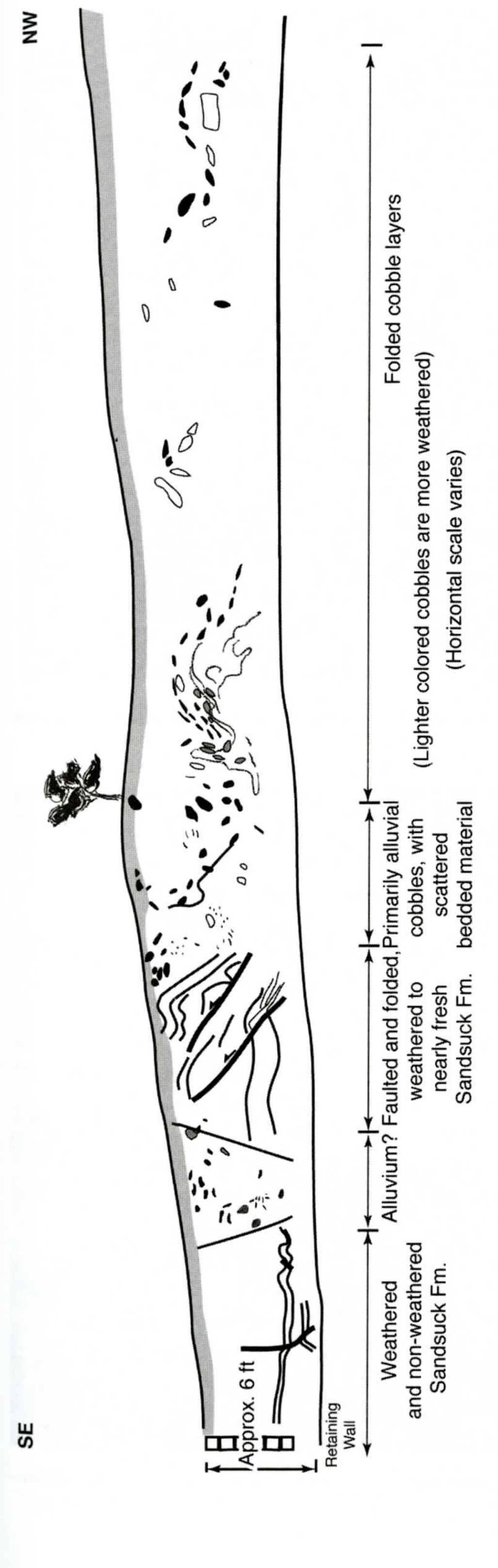


Figure 10. Cross section parallel to trench at Tellico Plains site located in figure 6. Older folded alluvium consists only of a small wedge on the right portion of the section.



posit pinched out over a very short distance perpendicular to the main cut and parallel to the trench (Figure 10).

The deposit was composed of two layers: a lower disturbed zone containing cobbles ranging from saprolitized angular graywacke fragments to fresh rounded vein quartz in a silt and clay matrix, and an upper undisturbed zone of rounded fresh cobbles and pebbles composed primarily of vein quartz (Figure 10). Most impressive in the disturbed zone was folded saprolite (Figure 11). These layers were folded with the long axes of pebbles and cobbles aligned parallel to each other and to manganese oxide and hematite stains that marked bedding in folded layers and outlined fold geometry (Figures 12 and 13). Based on measurements of cobble orientations within the five best defined folds of the cut face, fold axes were nearly horizontal and trended between 004 and 015 (Figure 14), with axial planes mostly vertical. These orientations are nearly perpendicular to the face of the road cut and the river valley. Sandsuck Formation saprolite formed the cores of the folds. This saprolite could have been forced into the core of a cobble layer as a rising mass of liquefied material or folded with the cobble layers. Offsets of these layers define small planar fault zones with <10 cm displacement that were located southeast of the primary deformed zone (Figure 14). The folds may have resulted from soft-sediment deformation and liquefaction triggered by a prehistoric earthquake. Alternatively, they could have been the product of dewatering and folding at the toe of a prehistoric landslide. With the possibility of human disturbance or other explanation for the deformation, however, more terrace deposits in the area need to be identified and investigated (Whisner and others, 2000).

DISCUSSION

No features were observed near Vonore, Ten-

Figure 11. Schematic drawing of the disturbed deposit in Tellico Plains, Tennessee. Photos in Figures 12 and 13 were made in the right third of the sketch.

Figure 12. Unscraped vertical face of Tellico Plains disturbed deposit. Box is location of Figure 13. Letters indicate cobble locations.

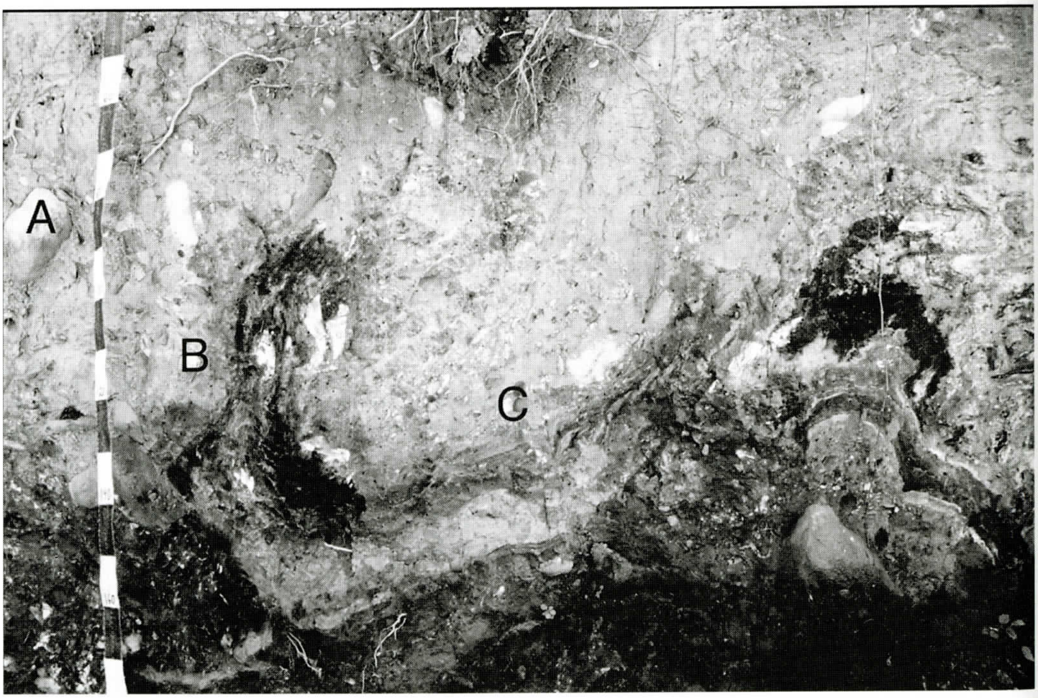


Figure 13. Scraped vertical face of Tellico Plains disturbed deposit. Letters indicate cobble locations in this photo and in Figure 12.

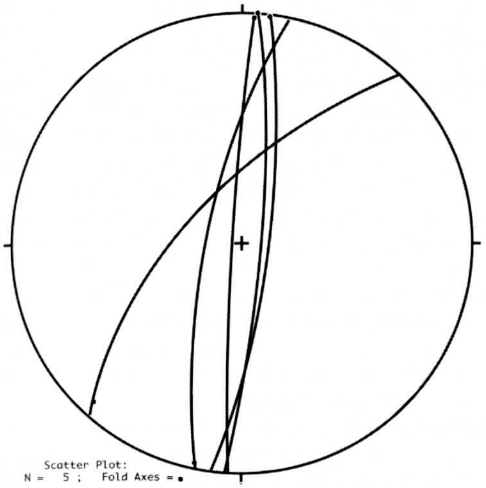


Figure 14. Lower hemisphere equal-area plots of orientations of folded cobble layers. The axes and axial planes of the five most prominent folds are shown.

nessee, that could be confidently attributed to a large earthquake. Many small faults and folds were observed during bedrock mapping, but these are all Alleghanian. Limited exposures of erosional remnants of higher terraces revealed no through going faults or clastic-filled fractures. Aerial photograph analysis combined with careful review of the Monroe County soil survey (United States Department of Agriculture, 1981) revealed no unusual surface features that could be described as earthquake related. Traverses along the banks of the Tellico River found nothing but flat-lying cobble layers and massive sand, silt, and mud deposits in the modern flood plain.

Research at the Gray fossil site does not currently emphasize structural or neotectonic investigations. Additional study of the Gray site may ultimately reveal a connection between the sand dikes and earthquake activity. If so, the ETSZ may have had a much greater extent and more lengthy history than is indicated by modern seismicity.

The Tellico Plains site, now removed by TDOT, exhibited potential liquefaction features. Only a small portion of the exposure was preserved, however, so the geometry, age, and extent of the folded beds remain unknown. The equivocal nature of the structures observed at this site and limited time it was available for study make finding another similar landslide or terrace deposit all the more important. Additional sites in the same area containing soft-sediment deformation would create a more compelling argument for an earthquake origin. Similar deposits of the same age, at similar elevations, have to date not been observed. The modern Tellico flood plain, but not smaller tributary streams, was traversed to identify disturbed sediments but none were found. Similar deposits along the Little Tennessee River contain only flat-lying, undisturbed fluvial deposits.

CONCLUSIONS

1. This is the first detailed geologic study in the ETSZ focused on trying to locate paleoseismic features. Some 300 km^2 of the most active part of the ETSZ (~1%) was mapped in detail without revealing concrete evidence of large prehistoric earthquakes. Many more square kilometers of unexplored stream valleys and terrace deposits that could entrain paleoseismic evidence exist in East Tennessee.
2. Clastic dikes in the small fault at the Gray fossil site could be evidence of prehistoric seismicity in an older, much more extensive ETSZ.
3. Folded and faulted pebble layers in an older landslide or terrace deposit beneath younger Tellico River alluvium at the Tellico Plains site could indicate early Holocene or late Pleistocene earthquake activity.

ACKNOWLEDGMENTS

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GEOCHEMICAL AND HYDROLOGIC CONSIDERATIONS ON EVOLUTION OF GROUNDWATERS IN A PORTION OF THE MISSISSIPPI EMBAYMENT

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ABSTRACT

Trace element geochemistry and numerical solute transport modeling indicate that groundwaters from the Paleozoic aquifer (Devonian and Lower Mississippian Iowa group) in a portion of the Mississippi Embayment obtained their present-day composition by fluid mixing and chemical weathering of exposed crystalline rocks. On first inspection, Cl-Br-Na relations suggest that present-day groundwater resulted from a simple dilution of seawater by freshwater. However, Li/Na, Ba/Na and Sr/Na ratios in groundwaters are significantly higher than those of seawater or Mississippi oil field brines, indicating that groundwaters must have obtained the excess lithophile elements from another source. Groundwaters have significantly higher $^{87}Sr/^{86}Sr$ ratios (0.7095-0.7097) than ancient Devonian-Mississippian seawater (less than 0.7080) or modern seawater (0.7090), again, suggesting an excess radiogenic elements source. Results of geochemical modeling show that normative salt composition of groundwaters is mainly a halite-dolomite-calcite assemblage, contrasting sharply with the predominantly halite-bischofite-carnallite-kieserite-anhydrite combination of normal seawater. Hydrologic simulations show that, without additional salt sources, seawater within the Paleozoic aquifer would have been significantly diluted by meteoric recharge in less than 0.5 m.y. The relatively high salinities and elevated trace and radiogenic element contents of the groundwaters could not have been derived solely from dilution of seawater. We propose that groundwaters were strongly affected by the chemical weathering and subsequent downward recharge of evaporated water in a closed basin. In our model, crystalline rocks were uplifted along the margins of the Mississippi Embayment in response to Permian Alleghanian/Ouachita orogenies. The hydrology and weathering of highlands yielded runoff with dissolved salt and trace elements, which subsequently washed into the Mississippi Embayment. Saline surface water, because of its high density, migrated downward and contaminated the underlying Paleozoic aquifer during the late Paleozoic.

INTRODUCTION

The origin of groundwaters and their dissolved solutes in sedimentary aquifers remains one of the most controversial problems in basin hydrology. Many explanations have been proposed to account for salinity in excess of that contained in original seawater buried with sediment. The "reverse osmosis" theory (Graf, 1982) postulates that the migration of ions (salt) is impeded by shales that act as semi-permeable membranes. Under sufficient hydrodynamic gradients, water molecules migrate upward across the membrane and cause the formation of more saline solutions at depth. Carpenter et al. (1974) proposed that metal-rich brines in the central Mississippi salt dome basin are mainly evaporated seawater originally trapped in salt. These "bittern" brines subsequently migrated into adjacent strata by compaction process. The oxygen and hydrogen isotopic compositions of brines also support that they originated as evaporated seawaters (Kharaka et al., 1987). Stueber and Walter (1991) suggested that some brines in sedimentary basins are simply remnant evaporated seawater as hydrodynamic drive may not be sufficient to displace deep dense brines. Alternatively, the elevated salinity might also have formed by dissolving evaporite beds by migrating groundwaters. Land and Prezbindowski (1981), for example, suggested that shallow brines in south-central Texas formed mainly by dissolving halite. Finally, the salinity could have arisen from infiltration of brines concentrated from evaporation of surface water in a closed basin. Carpenter and Trout (1978) found similarity in the bromide compositions of brines from the Smackover Formation in Arkansas and the present-day composition of the Dead Sea, suggesting that brines might have formed in closed basins in the southeast United States. Because of their high density, brines in the surface could have migrated downward into the basin, displacing pore fluids and ponding at depth.

The salinity level and chemical evolution of groundwaters from the Paleozoic aquifer in northeastern Mississippi is especially problematic. This aquifer is exploited for large quantities of drinking water at shallow depths, but chloride contents increase dramatically downdip. Chloride typically ranges from 100 to more than 10,000 mg/kg (Jennings, 1994), which is significantly higher than in groundwaters from younger coastal aquifer systems elsewhere in the southeastern United States (Lee, 1985; Lee and Strickland, 1988). High level of pumping of groundwaters from the Paleozoic aquifer has necessitated an evaluation of the origin of salinity and trace elements for groundwater supply in this region.

In northeastern Mississippi, saline groundwaters occur in the deep Paleozoic aquifer where salt beds are not present or have not been discovered. There has been no convincing explanation of the origin of salinity in the Paleozoic aquifer, which has been consistently flushed by freshwater recharge at least since the Pliocene. Given the current hydrologic condition, one would expect high levels of dissolved chloride to have been removed long ago. Wasson and Tharpe (1975) proposed that the high salinity of groundwater in the Paleozoic aquifer may be the result of pumping-induced leakage of groundwater from deeper strata. Jennings (1994) suggested that the aquifer had experienced repeated episodes of seawater recharge that mixed with meteoric water. Saunders and Swann (1991), however, based on the overall chloride budget of groundwaters, argued that they have been significantly influenced by fluid sources many times more saline than seawater.

For this study, a suite of groundwater samples from the Paleozoic aquifer in northeastern Mississippi were analyzed for their major ion and isotopic concentrations. Seven of those samples were analyzed for their trace element compositions using inductively coupled plasma-mass spectrometry (ICP-MS). Chloride, bromide, and sulfate concentrations were measured in the laboratory using a Dionex 2000 ion chromatography. Precision of anion analyses is ±1% for chloride and sulfate, and ±3% for bromide. A few samples were also analyzed for their $^{87}Sr/^{86}Sr$ ratios using a NBS surface emission mass spectrometer. Stable isotopes (^{18}O and ^{2}H) analyses were conducted at the University of Utah using the standard CO_2 equilibrium method. The precision limits are ±0.2 ‰ for ^{18}O and ±2 ‰ for ^{2}H. Data are used to interpret the origin of salinity and chemical evolution of the groundwaters by comparison with dilution trends of seawater and Mississippi oil field brines. Sr isotope ratios of groundwater are compared to those of seawater evolved in geologic time. In addition, the normative salt assemblage of groundwaters was calculated from the solute concentration assuming complete evaporation. Because river waters, seawater, and basin brines have distinctive salt assemblages (Bodine and Jones, 1986, 1990; Bodine and Andeholm, 1996), the representative normative salt composition of groundwaters provides additional geochemical constraints on their sources and diagenetic history.

Although geochemical data can place compelling constraints on hypothesized processes for the chemical evolution of groundwater, further constraints may be provided by quantitative reconstruction of the hydrologic history of a basin. Recent studies concerning fluid migration in sedimentary basins have demonstrated the utility of quantitative modeling techniques in understanding fluid flow, heat transfer, and sediment diagenesis (Bethke, 1989; Person et

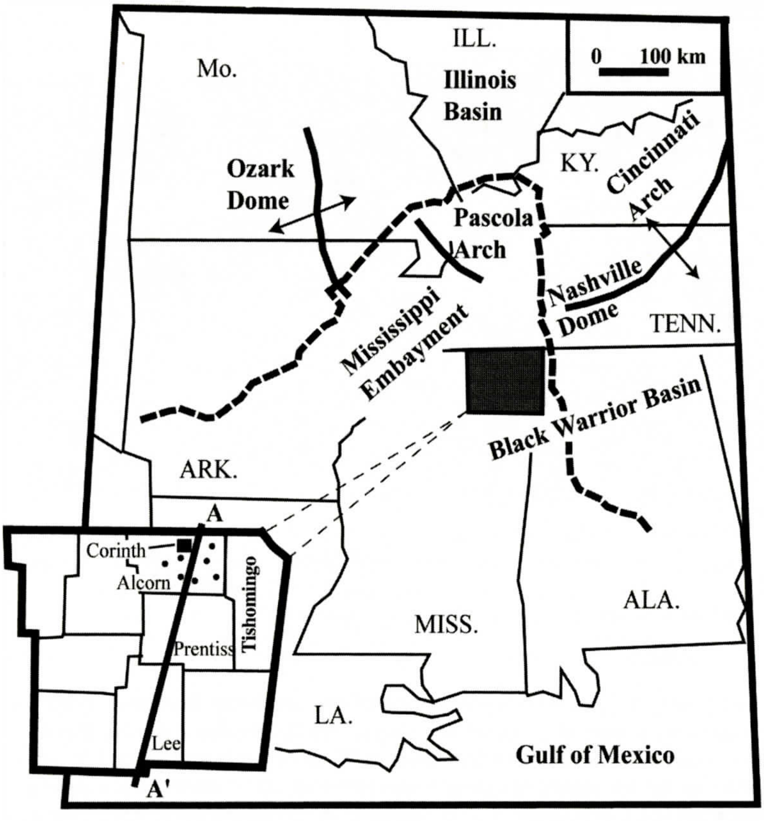

Figure 1. Simplified location map of study area (solid box) in northeastern Mississippi and surrounding areas. Solid dots show the locations of municipal wells in the Alcorn County.

al., 1996; Lee and Williams, 2000). However, there have been relatively few attempts to use transport theory to model salt transport in basin strata. In this study, we apply solute transport models to study the dilution of saline groundwater in the Paleozoic aquifer by freshwater incursion. The results of hydrologic modeling are integrated with geochemical data to interpret the origin of salinity and chemical evolution of groundwaters in the Paleozoic aquifer of northeastern Mississippi.

GEOLOGIC SETTING

Northeastern Mississippi is underlain by Upper Cretaceous sediments that dip to the west and unconformably overlie south-southwest dipping Paleozoic units. Paleozoic rocks are part of the Black Warrior basin which extends across Mississippi, Alabama, and Tennessee (Figure 1). The Black Warrior basin was part of a open marine embayment that subsided slowly throughout most of the Paleozoic. Subsidence ceased during the late Paleozoic as South America and Africa collided and the southeastern margins of North America became tightly sutured. The collision resulted in Alleghenian/Ouachita orogenies and the accompanying uplift of the Pascola arch (McKeown et al, 1990), which separated the Illinois basin to the north from the Black Warrior and Arkoma basins to the south. Kolata and Nelson (1990) suggested that the uplift of the Pascola, cresting in northwestern Tennessee and southeastern Missouri (Figure 1), probably persisted from Permian to Late Cretaceous time, prior to the subsidence of the modern Mississippi Embayment. The tectonic deformation of Pascola arch had exposed the Paleozoic sediments in the study area and caused a hiatus of deposition from late Pennsyl-

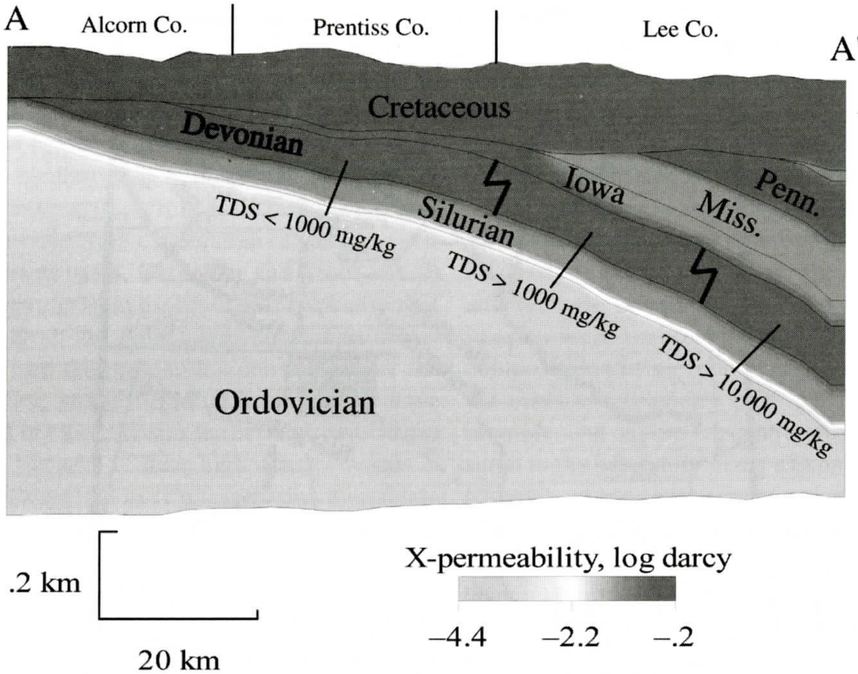

Figure 2. Cross section A-A' used in simulations of groundwater flow and salinity distribution in northeastern Mississippi (modified after Jennings, 1994). Section extends about 110 km across Alcorn, Prentiss, and Lee counties in northeastern Mississippi (see Figure 1 for location). Shades map permeability of basin strata ranging from $10^{-4.4}$ to $10^{-0.2}$ darcy. Permeable Devonian and Lower Mississippian Iowa group are major aquifers in the study area. Also shown are the levels of total dissolved solids (TDS) of groundwaters observed in the Devonian aquifer.

vanian to late Cretaceous time (Jennings, 1994). The late Cretaceous subsidence of the Mississippi Embayment resulted in the resumed deposition of about 500 to 1000 ft of Cretaceous sandy sediments (Jones, 1973) over the Paleozoic rocks (Figure 2). The Mississippi Embayment continued to subside and receive siliciclastic sediments over large areas during early Tertiary time (Kolata and Nelson, 1990). The northeastern Mississippi region probably assumed its present configuration (Figure 2) with the latest tectonic deformation of the Mississippi Embayment. The timing of the latest deformation is controversial, but Kolata and Nelson (1990) indicated an uplift during Pliocene time, as evidenced by the widespread Pliocene Grover Gravel deposits in the region. The latest uplift caused the sub-aerial exposure of Paleozoic and Cretaceous sections and subsequent development of the modern freshwater recharge system.

GROUNDWATER GEOCHEMISTRY

Major Ions and Stable Isotopes

Seven samples of groundwater from the Paleozoic aquifer of northeastern Mississippi were analyzed for concentrations of major and trace elements (Tables 1 and 2). Those water samples were collected from several high capacity municipal wells in the city of Corinth, Mississippi (Figure 1). Groundwater from the Paleozoic aquifer exhibits different geochemical characteristics common to many southeastern Coastal Plain groundwaters (e.g. Lee, 1985; Lee and Strickland, 1988; Floesser, 1996) even though it is hydraulically connected to the Coastal Plain aquifers (e.g., Jennings, 1994). Na-Cl relations generally show a close correspondence with the seawater dilution and halite dissolution trends (Figure 3A). The parallel increase in Na and Cl suggests that a conservative

Table 1. Chemical and isotopic compositions of groundwater from the Paleozoic aquifer. Ca and Sr concentrations are shown in Table 2

Sample ID#	Mg mg/kg	Na mg/kg	K mg/kg	Cl mg/kg	SO_4 mg/kg	Li µg/kg	Ba µg/kg	Br µg/kg	pH	Alkalinity mg/kg	$\delta^{18}O$ (‰)	δD (‰)
CO-5	10.8	80.3	7.0	110	10.9	205	333	798	7.8	115	-5.5	-29
CO-8	6.3	41.7	4.0	73	7.7	127	127	220	8.0	123	-	-
CO-13	9.9	42.1	5.5	70	8.9	123	317	454	7.4	113	-5.3	-30
CO-14	7.8	89.9	6.4	110	8.9	251	171	336	7.9	116	-5.4	-29
CO-15	7.5	51.5	5.3	73	7.7	153	277	209	7.6	113	-4.7	-30
CO-16	10.1	64.8	6.2	100	8.6	196	343	321	7.7	118	-5.4	-30
CO-17	10.2	64.8	6.4	130	10.4	202	309	323	7.8	114	-5.7	-31

Table 2. Sr isotope compositions and Sr and Ca concentrations of selected rocks, natural waters, and groundwater samples from the Paleozoic aquifer, northeastern Mississippi

	Ca (mg/kg)	Sr (µg/kg)	Sr/Ca-molar	$^{87}Sr/^{86}Sr$
CO-5	38.82	1336	0.01572	0.7096[1]
CO-8	20.45	668	0.01494	-
CO-13	25.60	1020	0.01819	0.7095[1]
CO-14	29.02	956	0.01503	0.7097[1]
CO-15	29.40	969	0.01504	-
CO-16	31.20	1264	0.01849	0.7097[1]
CO-17	40.73	1614	0.01809	-
Seawater	411	8000	0.00886	0.7065-0.7090[2]
Rivers[3]	1.4-183	10-160	0.001-0.007	0.7077-0.7155
Brines[3]				0.7079-0.7230
Young volcanic rocks[4]				0.7040
Old silicate rocks[4]				0.720
Marine carbonate rocks[4]				0.708

1. Adjusted according to NBS 987 Sr standard for comparative purposes, this study
2. Modern seawater = 0.7090 (Drever, 1997)
3. North American rivers from Goldstein and Jacobsen (1987)
4. Faure (1986)

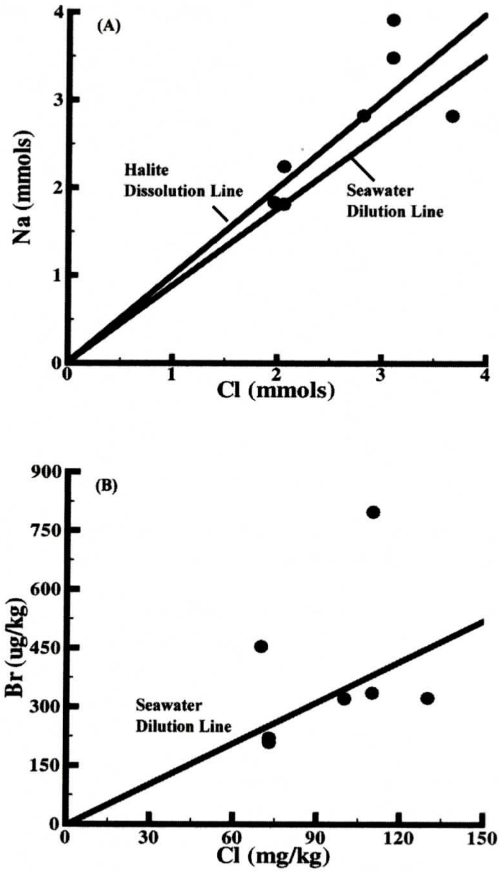

Figure 3. (A) Na-Cl and (B) Br-Cl in groundwater samples from the Paleozoic aquifer, northeastern Mississippi. The points are observed groundwater compositions. The seawater dilution trend represents simple physical (conservative) mixing of freshwater with seawater (Na^+ = 10,760 mg/kg; Cl^- = 19,350 mg/kg; Br^- = 67 mg/kg). Halite dissolution results in an equimolar gain in Na^+ and Cl^-. Meteoric dilution drives the trend toward the origin.

dilution process has subsequently affected these waters. Points lying significantly above the seawater dilution trend, if not the result of analytical error, may be attributed to dissolution of halite followed by meteoric dilution. Points below the conservative mixing line may be explained by Na^+ exchange or fixation on clays. Dissolved Na^+ can be removed from solution through cation exchange with clay minerals during the displacement of seawater by freshwater (e.g., Chapelle and Knobel, 1983; Appelo, 1994).

Cl/Br ratios (Table 1) were used to determine the source of salinity in groundwater from the Paleozoic aquifer. Different Cl/Br ratios have been observed in various natural waters (Davis et al., 1998) including atmospheric precipitation (50-150), seawater and evaporated seawater (~290), and deep basin brine affected by congruent halite dissolution (>1,000). The Cl/Br ratios of water samples range from 135 to 400, with an average of 290 (Table 1). The range indicates that the groundwater has been influenced mostly by fresh water incursion and seawater evaporation, although some input from congruent halite dissolution cannot be completely ruled out. Figure 3B shows the Cl/Br ratios of groundwater relative to the seawater dilution trajectory (Carpenter, 1978). The origin and processes affecting salinity can be determined by the Cl/Br relationship to this trajectory. Cl/Br ratios remain constant during seawater evaporation until halite saturation is achieved, at which point Br is concentrated in the remaining solution, while Cl is removed by halite precipitation (Connolly et al., 1990). As a result, the Cl/Br ratio of the remaining brine decreases progressively during halite precipitation. Saline groundwaters derived from remnant evaporated brines beyond halite saturation generally exhibit Cl/Br ratios lower than seawater (i.e., to the right of the seawater evaporation and dilution trajectory) while congruent halite dissolution can produce groundwater with higher Cl/Br ratios (i.e., to the left of the seawater evaporation trajectory). Five water samples of the Paleozoic aquifer plot slightly to the right of the trajectory (Figure 3B), indicating that they acquired salinity from remnant evaporated brines, rather than congruent dissolution of halite. However, dissolution of halite is more likely a salinity source for two water samples (CO-5 and CO-13) plotted above or to the left of the trajectory.

Total dissolved solids (TDS) of the Paleozoic formation waters, ranging up to over 10,000 mg/kg, however, are significantly higher than in groundwaters from younger coastal aquifers elsewhere in the southeastern Coastal Plain. For example, younger Tertiary Florida carbonate

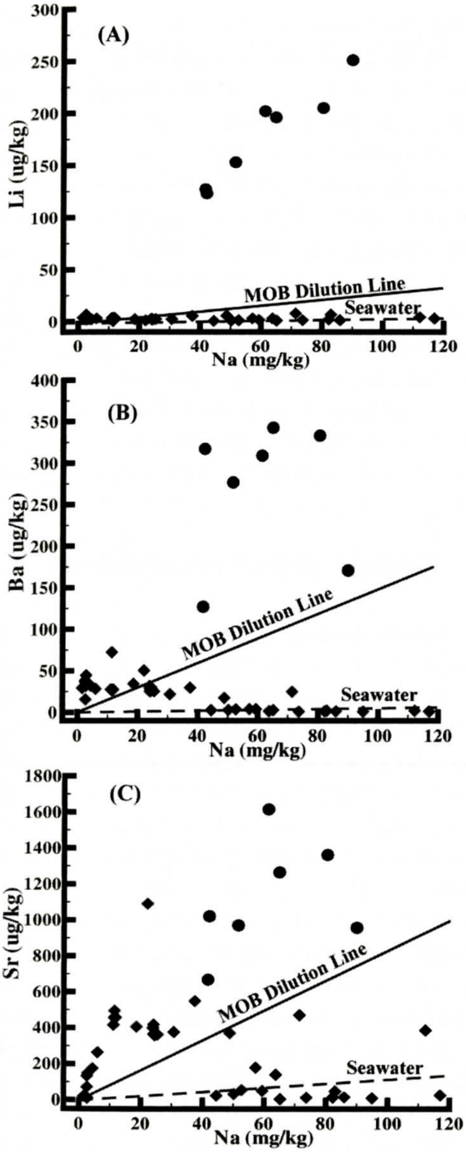

Figure 4. (A) Li-Na, (B) Ba-Na, and (C) Sr-Na relations in groundwater samples from the Paleozoic aquifer (solid circles) in northeastern Mississippi (this study) and from the Cretaceous coastal aquifers in the region (diamonds; Floesser, 1996). Groundwaters from the Paleozoic aquifer and from the coastal aquifers have distinct and separate trends. The linear lines represent dilution trends of seawater (dashed line) and Mississippi oil field brine (MOB) (solid line). Data points representing groundwaters from the coastal aquifers plot very close to the seawater or the MOB dilution trends. Waters from the Paleozoic aquifer in northeastern Mississippi, however, reveal a significant gain of Li, Ba, and Sr, relative to the seawater dilution trend.

aquifers have Cl contents less than 20 mg/kg (Back and Hanshaw, 1970). Shallow Cretaceous coastal plain aquifers in Alabama have Cl contents less than 100 mg/kg (Cook, 1993). The Paleozoic aquifer has been subjected to freshwater recharge since the latest tectonic uplift during the Pliocene (about 5 m.y. ago). Given the long-standing freshwater infiltration, the salinity should have been largely removed. Without known salt sources, the chloride content of the groundwaters in the Paleozoic aquifer is problematic and not easily explained.

Trace Element Geochemistry

Plots of Li^+, Ba^{2+}, and Sr^{2+} vs. Na^+ show that these elements are greatly enriched relative to the dilution trends of seawater and Mississippi oil field brines (Figure 4). Elevated concentrations of trace elements lithium, strontium, and barium are apparently controlled primarily by chemical weathering of crustal rocks rather than by mixing of freshwater with seawater. Average concentrations of lithium, strontium, and barium in crustal rocks such as granite could reach as much as 30, 250, and 600 mg/kg, respectively (Drever, 1997). Trace elements in those rocks dissolve readily when weathering is intense (i.e. in a humid climate). For example, the Ganges-Brahmaputra river draining the rapidly weathering Himalayan mountain belt can carry substantial trace metal flux. Average concentrations of strontium and barium in groundwater of the Ganges-Brahmaputra river basin are 450±300 and 178±135 μg/kg, respectively (Dowing et al., 2003). In addition, groundwater from the Cretaceous coastal plain aquifers in central-south Alabama also contains elevated strontium and barium concentrations up to several hundreds of μg/kg (Penny, et al., 2002). Simple weathering of normal crystalline rocks, coupled with subsequent adorption and desorption processes, could lead to the enrichment of Sr and Ba in groundwaters hosted by coastal plain aquifers. Elevated metal concentrations found in modern salt lakes with evaporite deposits (see review by Hem, 1985) further support the concept that lithophile elements may be derived from the intense weathering of rocks in a tropical or subtropical climate. Because of the buoyant forces exerted by their high density, brines in salt lakes may migrate downward and contaminate underlying groundwaters. High trace-element concentrations of groundwaters in some sedimentary basins (Moldovanyi and Walter, 1992; Stueber et al., 1993) may also be derived from the infiltration of a surface brine.

Alternatively, trace elements may be released into solution by chemical interaction between seawater and crustal rocks in marine environments (i.e., Bower, 1989). Groundwater samples in the study area range in $\delta^{18}O$ from -5.7 to -4.7 ‰ and δD from -31 to -29 ‰ relative to SMOW (Table 1). These values resemble those of surface water and are significantly lower than those of seawater or evolved seawater, which are normally close to 0 ‰ or higher. The low stable isotopic ratios of groundwater appear incompatible with a marine origin, and therefore, preclude the possibility that trace elements were derived solely from interaction between seawater and crustal rocks.

Strontium Isotopic Compositions

Strontium isotope ratios of four groundwater samples were measured at the High Magnetic Field Laboratory at Florida State University using a NBS surface emission mass spectrometer. All groundwater samples have significantly higher $^{87}Sr/^{86}Sr$ ratios (0.7095-0.7097) than Devonian-Mississippian seawater (less than 0.7080) and modern seawater (0.7090) (Table 2). The radiogenic Sr in the groundwater was likely derived through chemical weathering of exposed crustal rocks. The average $^{87}Sr/^{86}Sr$ ratio of old crustal rocks with silicate composition is about 0.720 (Brass, 1976), significantly higher than seawater. The radiogenic Sr was less likely derived through interaction of groundwater with carbonate rocks along the flow path since the average $^{87}Sr/^{86}Sr$ ratio of marine carbonate rocks, about 0.708 (Faure, 1986; McCauley and DePaolo, 1997), is lower than those of groundwater. It is also unlikely that the radiogenic Sr was derived from seawater modified by evaporation, because evaporated seawater will bear the same $^{87}Sr/^{86}Sr$ ratios as the original seawater (Banner et al., 1988). The Sr/Ca molar ratios of groundwater (0.0150-0.0185) in the study area are also significantly higher than that of seawater (0.0088) and North American river water (0.001-0.007) (Table 2), further suggesting that the present-day groundwaters from the Paleozoic aquifer could not have been derived solely by dilution of seawater by surface water. The strontium concentrations and isotope compositions clearly indicate that groundwaters must have obtained the excess radiogenic elements from another source. The significant enrichment of radiogenic Sr could be attributed to chemical weathering of crustal rocks uplifted during Permian Alleghanian/Ouachita orogenies.

Normative Salt Assemblage

Transformation of solute concentrations of natural waters into equilibrium salt assemblages may provide insights into their source and diagenetic history. The geochemical modeling computer program SNORM (Bodine and Jones, 1986) was used to calculate the normative salt assemblage from the solute concentration of groundwaters, assuming complete removal of water by evaporation. Table 3 shows that calculated salt assemblages of seven groundwater samples collected from the Paleozoic aquifer, seawater, and evaporated brines in a modern salt lake. The Paleozoic groundwaters are characterized by normative halite-dolomite-calcite salts and minor Li, Ba, Sr salts. Although their halite salt reflects an origin of marine-like water, the halite-dolomite-calcite assemblage, is markedly different from normal seawater or evaporated seawater, which are predominantly halite-bischofite-carnallite-kieserite-anhydrite (Table 3). Evaporated brines in modern salt lakes such as the Bristol Dry Lake (in California; Table 3) and the Great Salt Lake (not shown) also contain minor lithophile-element salts, but generally do not contain carbonate salts. The distinctive carbonate salt assemblage of Paleozoic groundwaters can be considered as meteoric-weathering origin from dissolution of carbonate or Ca-Mg silicate minerals in acid meteoric waters, or alternatively, by chemical

Table 3. Normative salt assemblage (in mole %) of seawater, salt lake, and groundwater samples from the Paleozoic aquifer, northeastern Mississippi

Salt norm	Formula	Groundwater Sample[1]								
		CO-5	CO-8	CO-13	CO-14	CO-15	CO-16	CO-17	Seawater[2]	Bristol[3] Dry Lake
Halite	$NaCl$	76.11	72.12	61.40	79.93	71.16	70.85	68.70	88.05	67.98
Dolomite	$CaMg(CO_3)_2$	9.84	12.37	12.31	7.65	10.78	9.35	6.49	-	–
Calcite	$CaCO_3$	10.96	5.30	17.78	3.29	11.96	12.68	15.44	-	–
Magnesite	$MgCO_3$	-	-	-	-	-	-	-	0.22	–
Sylvite	KCl	1.07	0.93	3.40	0.69	0.80	2.68	-	-	1.10
Antarcticite	$CaCl_2.6H_2O$	-	-	-	-	-	-	-	-	29.36
Bischofite	$MgCl_2.6H_2O$	-	-	-	-	-	-	-	4.48	–
Kieserite	$MgSO_4.H_2O$	-	-	-	-	-	-	-	3.35	-
Anhydrite	$CaSO_4$	-	-	2.88	-	2.06	2.05	2.52	1.93	0.06
Pirssonite	$Na_2Ca(CO_3)_2.2H_2O$	-	6.82	-	6.43	2.88	-	-	-	-
Carnallite	$KMgCl_3.6H_2O$	-	-	1.31	-	-	1.07	4.15	-	1.20
Aphthitalite	$K_3Na(SO_4)_2$	0.78	1.32	-	1.08	1.31	-	1.25	-	-
Indirite	$Mg_2B_6O_{11}.15H_2O$	-	-	-	-	-	-	-	0.01	–
Syngenite	$CaK_2(SO_4)_2.H2O$	0.26	-	-	-	-	-	-	-	-
Celestite	$SrSO_4$	0.34	-	-	-	-	-	-	0.02	–
Fluorite	CaF_2	0.25	-	0.15	-	-	0.33	0.18	-	–
Barite	$BaSO_4$	0.06	0.04	0.08	0.03	0.07	-	-	-	–
Strontianite	$SrCO_3$	-	0.37	-	0.26	-	0.06	-	-	–
	$Li_2SO_4.H_2O$	0.33	0.17	0.30	0.23	0.10	0.36	-	-	–
	$LiCl.H_2O$	-	-	-	-	-	-	0.74	-	-
	LiF	-	0.54	-	0.41	0.55	-	-	-	–
	$SrCl_2.6H_2O$	-	-	0.39	-	-	0.36	0.47	-	0.30
	$BaCl_2.H_2O$	-	-	-	-	-	-	0.06	-	-

[1] groundwater samples collected from various municipal wells in the city of Corinth, Mississippi

[2] also contain 0.006 % mol of Sellaite (MgF_2), 0.002 % mol of $Li_2SO_4.H_2O$, 0.0004 % mol of Wagnerite ($Mg_2(PO_4)F$), and 0.00002 % mol of Barite ($BaSO_4$).

[3] chemical analysis from White et al. (1963), Table 27.

interaction between migrating groundwaters and carbonate minerals. Diagenetic alterations such as calcite dissolution and precipitation of Fe-Mn carbonate, for example, have been observed in the Paleozoic aquifer (Saunders and Swann, 1992). Normative pirssonite (samples CO-8,14,15) can result from weathering of alkali/alkaline-earth silicate minerals (feldspar, pyroxene, and amphibole). The presence of alkali sulfates such as aphthitalite (CO-5,8,14,15,17), barite (CO-5,8,13,14,15), and alkali-calcium salt syngenite (CO-5) can represent sulfuric-acid weathering of silicate minerals. The presence of several Li, Ba, and Sr salts suggests that groundwaters have obtained lithophile elements from a crustal source, most likely through chemical weathering of exposed crystalline rocks or shales. The representative salt assemblages thus reflect multiple origins of water and various weathering and diagenesis processes.

SOLUTE TRANSFER MODELING

We used the numerical model Basin2 (Bethke et al., 1993) to simulate the dilution of saline groundwater in the Paleozoic aquifer by freshwater incursion along a north-south cross section in the study area (Figure 2). The Basin2 model calculates groundwater flow that arises from sediment compaction and topographic relief, the transfer of heat by conduction and advecting groundwaters, and solute transfer by advection and hydrodynamic dispersion. The program calculates the distribution and transport of a solute in a groundwater system by solving the equation

$$\frac{\partial}{\partial t}(\phi C) = \nabla \cdot (\phi D \nabla C) - \nabla \cdot (qC) \tag{1}$$

where C is concentration (mol/cm^3) of a nonreactive solute, ϕ is porosity, q is specific discharge (cm/sec), and D is the tensor for the processes of hydrodynamic dispersion, which accounts for molecular diffusion of solutes as well as mechanical dispersion. The model calculates the coefficients of hydrodynamic dispersion D_x and D_z from

$$D_x = D^* + \alpha_L v_x + \alpha_T v_z \tag{2}$$

and

$$D_z = D^* + \alpha_L v_z + \alpha_T v_x \tag{3}$$

Here D^* is the diffusion constant (cm^2/sec), v_x and v_z are lateral and vertical groundwater velocities (cm/yr) in curvilinear coordinates, and α_L and α_T are the dispersivities (cm) in the longitudinal and transverse directions (or along and across the direction of flow). According to equations (2) and (3), the effect of dispersion is proportional to the flow velocity. Diffusion is the only mass transfer process under no flow conditions. Because the diffusion coefficient is relatively small (less than about 10^{-6} cm^2/sec) compared to dispersivities (Freeze and Cheery, 1979), the effects of dispersion dominate those of diffusion at even modest flow rates (> 10^{-6} cm sec^{-1} or a few meters per year). For the purpose of hydrologic analysis, strata in the study area are divided into 6 hydrostratigraphic units: (1) Ordovician-Silurian, (2) Devonian, (3) Lower Mississippian, (4) Upper Mississippian, (5) Pennsylvanian, and (6) Upper Cretaceous. The Ordovician-Silurian unit consists primarily of carbonate rocks (Henderson, 1991). This unit has low porosity and permeability but secondary porosity may be developed locally by the dissolution of carbonate by infiltrating freshwater (Jennings, 1994). The Devonian unit consists of chert and cherty limestone, serving as the main water supply aquifer from the Paleozoic rocks in northeastern Mississippi. The Lower Mississippian unit, known as Iowa group, consists of chert, shale, and carbonates. Porosity and permeability are generally low in this unit due to cementation and compaction. High porosity and permeability is restricted primarily to outcrops containing highly weathered and fractured chert units. The Pennsylvanian unit contains a thick sequence of sandstones, conglomerates, and shales (Thomas, 1988). The Upper Mississippian unit consists mainly of sandstones, shales, and limestones. Gas and oil test wells indicate low permeability in these rocks.

Figure 2 shows the reconstructed cross-section and hydrostratigraphy used in the simulation. The calculation accounts for advection driven by topographic relief and buoyant (density) forces and mass (salt) transfer. The initial salinity of groundwater in all basin strata is set to 0.5 molal, assuming down-to-basin infiltration of seawater during the subsidence of the Mississippi Embayment prior to Pliocene. The salinity along the basin surface is set to zero when the section emerges above sea level and is exposed to rainwater, following the latest Pliocene uplift of the region. The transient simulation spans a period of 0.5 m.y. as the section is exposed to freshwater recharge. The permeability of the Upper Cretaceous strata is set to a constant value of 0.5 darcy, which represents the low end of the field aquifer test data (0.5 to 50 darcy, Wasson and Tharpe, 1975). The choice of lower limit of permeability value poses the most stringent test of the model because it assumes relatively poor hydraulic connection between Paleozoic aquifer and the shallowest

Table 4. Correlations used in the hydrologic simulations to calculate porosity and permeability of Paleozoic strata

	Porosity*			Permeability**		
	ϕ_0	b (km^{-1})	ϕ_1	A	B	k_x/k_z
Sandstone	0.40	0.50	0.05	15	-3	2.5
Shale	0.55	0.85	0.05	8	-7	10
Ordovician carbonate	0.40	0.55	0.05	6	-6	2.5
Devonian carbonate	0.40	0.50	0.05	15	-3	2.5

*$\phi = \phi_0 \exp(-bZ) + \phi_1$, expressed as a fraction; Z is burial depth (km).

**$\log k_x$ (μm^2) $= A\phi + B$; $k_x \leq 1\ \mu m^2$; $1\ \mu m^2 \cong 1$ darcy.

Cretaceous strata. The goal is to estimate the maximum time required for freshwater recharge to dilute the saline groundwater in the Paleozoic aquifer. The Paleozoic stratigraphic unit in the calculations is composed of varying fractions of four rock types: sandstone, shale, Ordovician carbonate, and Devonian carbonate (aquifer). We calculate the evolution of porosity and permeability of each rock buried, using correlation shown in Table 4. The diffusion coefficient D^* is assumed to be 1.5×10^{-5} cm^2/sec; and the longitudinal dispersivity (α_L) and transverse dispersivity (α_T) are 500 cm and 50 cm, respectively. The simulation allows us to evaluate the time required for the dilution and displacement of saline formation waters in Paleozoic aquifer by freshwater recharge from the overlying Cretaceous section. The results can be compared to observed salinity level (ranges from several hundreds mg/kg to more than 10,000 mg/kg; Figure 2), thereby providing important constraints on the origin of salinity in the aquifer.

Figure 5 shows the calculated flow regime and the distribution of salinity in the cross section after 0.05 and 0.5 m.y., respectively, of freshwater infiltration. The topographic relief across the basin surface provides the drive for a regional flow regime and downward recharge of freshwater. The calculation results show that salinity of 'seawater' within the Devonian aquifer can be reduced to less than 1,000 mg/kg by meteoric recharge for a short interval of less than 0.5 m.y. (Figure 5). Because the present freshwater recharge has probably existed since early Pliocene (for at least 5 m.y.), the salinity would have been removed long ago without additional solute sources. Thus, modeling indicates that the present-day salinity in the Paleozoic aquifer could not have been derived solely from dilution of seawater.

DISCUSSION AND CONCLUSIONS

In this study, we integrate geochemical constraints with quantitative models of groundwater flow and mass transport to explain the evolution of groundwaters in the Paleozoic aquifer in northeastern Mississippi. Our results suggest that groundwaters in the aquifer probably achieved their high salinity (up to 10,000 mg/kg) and trace-element concentrations through subsurface infiltration of evaporated water in a subtropical, closed basin with restricted circulation, similar to many modern analogues such as Dead Sea, Great Salt Lake (Utah), and Mono Lake (California). Late Paleozoic tectonic activities such as faulting could have produced isolated basins with internal drainage of little or no outlet in the region. In this model, crystalline rocks were exposed along the margins of the Mississippi Embayment during Permian Alleghanian/Ouachita orogenies. Weathered crustal rocks released trace elements into surface water which drained into the Mississippi Embayment, where evapo-

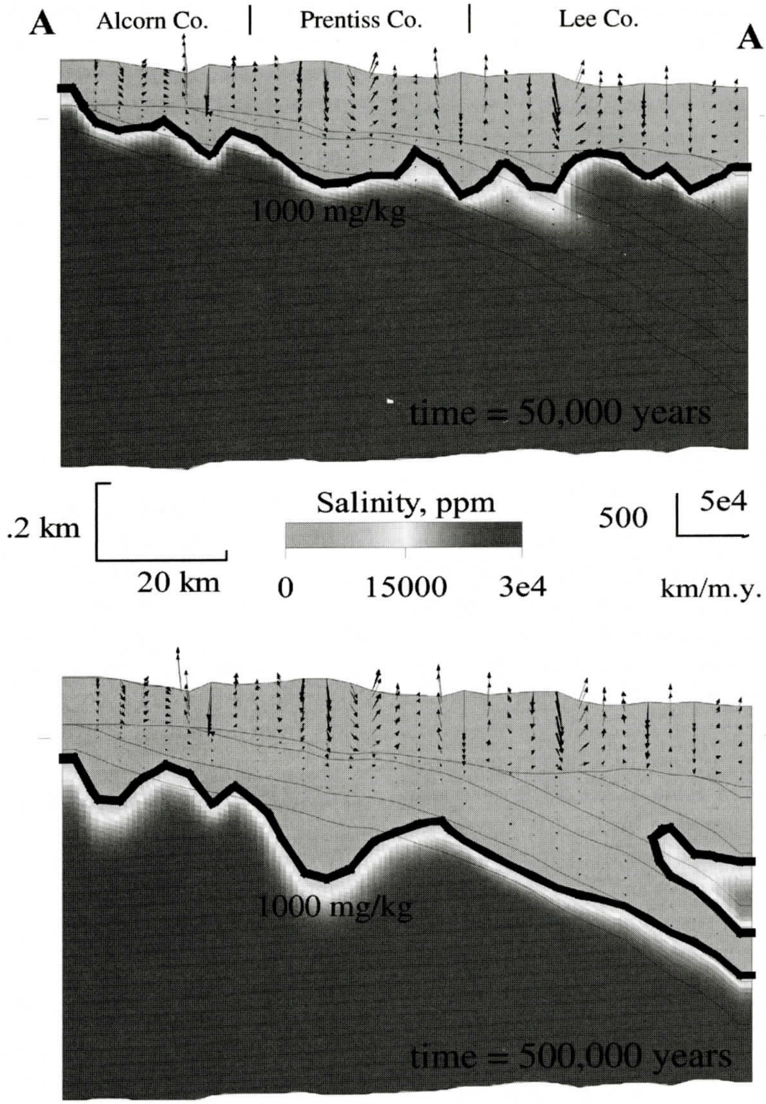

Figure 5. Predicted groundwater flow and salinity distribution along the cross-section in northeastern Mississippi after 0.05 (upper diagram) and 0.5 m.y (bottom diagram) of freshwater infiltration, respectively, following the latest uplift of the region during the Pliocene. Shades map salinity of groundwater ranging from 0 to 30,000 mg/kg. Arrows show predicted velocities of flow driven by topographic relief. Contour lines represent groundwater salinity of 1,000 mg/kg predicted by the model.

rated water subsequently infiltrated and contaminated the underlying Paleozoic aquifer (Figure 6). Typical crystalline rocks in the study area consist mainly of biotite, amphibole, feldspar, muscovite, and plagioclase. Biotite, amphibole, feldspar, and muscovite may contain significant amounts of trace elements including Sr, Ba, Li, Cr, Rb, and Mn (Levinson, 1974; Deer et al., 1992). Biotite contains the highest concentrations of trace elements and is one of the most easily weathered minerals (Pritchett, 1998). Our model can be further confirmed by chemical compositions of many natural brines in modern salt lakes or shallow groundwaters where high concentrations of lithophile elements have been founded. Lithium has been re-

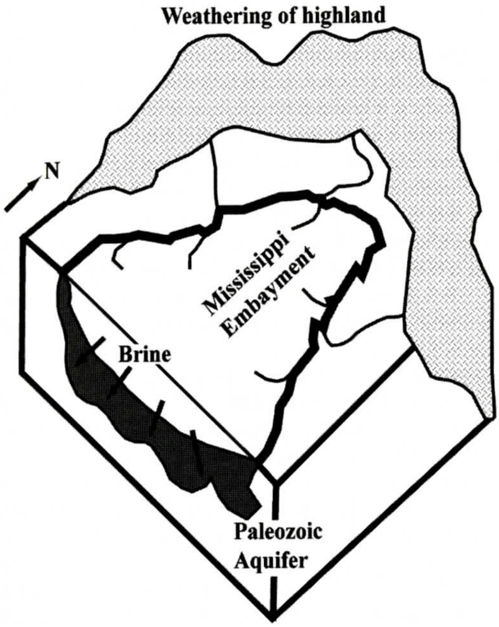

Figure 6. Schematic hydrologic environment of the MississippiEmbayment, following the Alleghanian/Ouachita orogenies during late Paleozoic time. Flow patterns show the infiltration of evaporated water into the underlying Paleozoic aquifer. Lithophile elements in water may be derived from the intensive weathering of uplifted crustal rocks.

covered commercially from natural brines and evaporites in Searles Lake, California (Hem, 1985). White et al. (1963) reported high concentrations of Sr (960 mg/kg) in Bristol Dry Lake (California) and Li (180 μg/kg) in Great Salt Lake (Utah). White et al. (1963) reported high Ba concentrations (up to 70 mg/kg) in California spring waters where sulfate reduction lowers the sulfate concentration and causes the barium to increase. Chemical weathering of the Himalayas, coupled with subsequent adsorption and depsorption reactions, leads to elevated Sr and Ba concentrations (up to several hundreds μg/kg) in both the groundwater and river water of the Bengal basin (Dowling et al., 2003).

Groundwaters in the study area are characterized by normative halite-dolomite-calcite salt assemblage with minor lithophile-element salts, which are markedly different from normal seawater or typical sedimentary hypersaline waters. This distinctive salt assemblage indicates a strong influence of chemical weathering and diagenesis in addition to fluid mixing. The influence of chemical weathering is also supported by the elevated Sr isotope ratios of groundwater with respect to seawater. Geochemists invoked that the dramatic increase of worldwide $^{87}Sr/^{86}Sr$ ratios in marine sediments from 0.7077 to 0.7092 over the last 40 million years as an indication of increasing chemical weathering of continental crustal rocks with high radiogenic Sr contents (Raymo et al., 1988). Edmond (1992) and Richter et al. (1992) argued that the rise of $^{87}Sr/^{86}Sr$ ratios reflects the intensive weathering of massive Himalayan-Tibetan plateaus and mountain belts through the Cenozoic. The Himalayan-Tibetan source rocks have high $^{87}Sr/^{86}Sr$ ratios near 0.742 (McCauley and DePaolo, 1997), leading to enriched radiogenic ^{87}Sr contents in the runoff of sediment-laden rivers to the ocean. We argue that enrichment of groundwater ^{87}Sr in part of the Mississippi Embayment could be attributed to enhanced chemical weathering of crustal rocks uplifted and unroofed during Permian Alleghanian/Ouachita orogenies. Our interpretations have implications for the origin of elevated trace elements in many alluvial aquifers that cause water supply and health problems in many places around the world (e.g., As-contaminated groundwater in Bangladesh and West Bengal, India). Although the transport of trace elements in shallow groundwater systems involves complicated sorption/desorption biochemical cycles (e.g., Nickson et al., 2000), the cycles could begin with natural weathering of crustal rocks in uplifted areas.

Hydrologic simulations suggest that groundwaters with seawater salinity can be significantly diluted by infiltrating meteoric water in less than 0.5 m.y in the study area. This result suggests that relatively high salinities in the present-day groundwaters from the Paleozoic aquifer could not have been derived solely by mixing of meteoric water with seawater, and that additional salt sources are required. Without additional salt beds, it is difficult to explain why the downdip portion of the Paleozoic aquifer has not been flushed to the extent expected given the duration of freshwater recharge and hydrodynamic characteristics of the basin.

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SELECTED SEDIMENT PROPERTIES OF QUATERNARY DEPOSITS, SHELBY COUNTY, TENNESSEE: IMPLICATIONS FOR CONTAMINANT HYDROGEOLOGY AND QUATERNARY STRATIGRAPHY

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ABSTRACT

Contaminant hydrology and stratigraphic characteristics of Quaternary sediments in Shelby County, Tennessee, were investigated using field observations and laboratory analysis of samples from five boreholes. Thirty-nine samples of Quaternary sediments and four samples of underlying Mid-Tertiary sediments were analyzed for grain size, organic carbon (OC) content, cation exchange capacity (CEC), and clay mineralogy. Three different Quaternary stratigraphic units are present: Pliocene(?)-Pleistocene fluvial-terrace deposits, Pleistocene loess, and Pleistocene and Holocene alluvium. Many of the measured sedimentary characteristics of the loess and fluvial-terrace deposits are significantly different from each other, especially if those of a transition zone in the upper part of the fluvial-terrace deposits are discounted. The sedimentary characteristics of the alluvium are generally intermediate between those of the loess and fluvial-terrace deposits, although the presence of some features, such as abundant vermiculite and large organic fragments, are unique to the alluvium. The variations in the sedimentary characteristics of a given Quaternary stratigraphic unit between the borehole sites are minor and generally are related to topographic position and age of deposits. The clay mineralogy of the Quaternary stratigraphic units is related to specific sources of sediment and weathering processes in the Mississippi Embayment. The CEC and OC values of the Quaternary deposits, in concert with hydrologic inference from grain-size characteristics, suggest that contaminant migration may be retarded during matrix infiltration through the loess and upper alluvium. The potential for contaminant migration in the fluvial-terrace deposits and lower alluvium is much greater owing to lower CEC and OC values and higher hydraulic conductivity in these units.

INTRODUCTION

Ground water is extracted from the Eocene-age Memphis aquifer for municipal water supplies in western Tennessee (Figure 1), and correlative aquifers in northern Mississippi and eastern Arkansas (Parks and Carmichael, 1990). Seepage from waste-disposal sites and industry as well as encroachment of urban development in the recharge area of the Memphis aquifer have heightened concerns regarding the vulnerability of this aquifer to contamination from near-surface sources (Graham and Parks, 1986; Parks, 1990). In order for contaminants to reach the Memphis aquifer, either in the recharge area or through windows in the upper Claiborne confining unit, the contaminants must pass through varying thicknesses of Pleistocene loess and Pliocene(?)-Pleistocene fluvial-terrace deposits and/or late Pleistocene-Holocene alluvium.

The purpose of this study is to evaluate sediment properties (grain size, cation exchange capacity, organic carbon content, and clay mineralogy) of the Quaternary deposits in Shelby County, and determine the degree to which certain properties retard contaminant transport

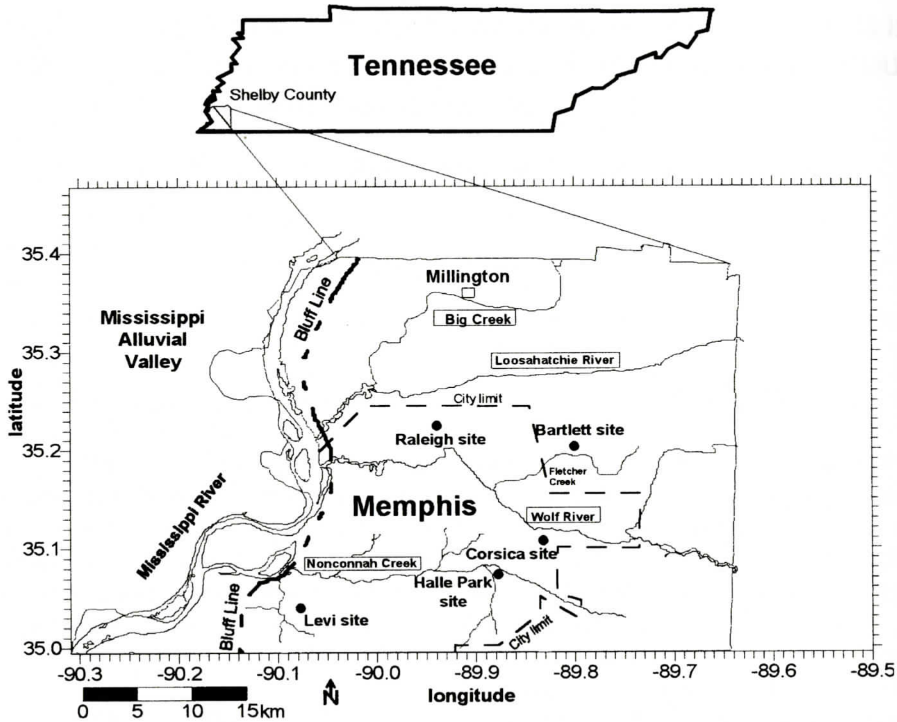

Figure 1. Map of Memphis and Shelby County, Tennessee, illustrating samples locations and other important features.

to the Memphis aquifer. Studies in other areas have found that contaminant migration in groundwater may be controlled by specific sedimentary and geochemical characteristics of units within stratigraphic successions (Heron and others, 1998; Warren and Rudolph, 1997). Grain-size distribution is closely related to porosity and hydraulic conductivity in unconsolidated sediments (Fetter, 2001; Kasenow, 1997), such as the Quaternary deposits in Shelby County, Tennessee. Cation exchange in sediments is an important mechanism for removal of dissolved contaminant metals, such as As, Pb, and Cr, from water (Smith and others, 1995; Langmuir, 1997). Organic carbon in soils and sediments is important as a sorption media for slightly water soluble, non-polar contaminant organic compounds, such as benzene and trichloroethylene (Karickhoff and others, 1979; Allen-King and others, 1997; Kehew, 2001). Clay mineralogy partially determines cation exchange capacity and selectivity (Moore and Reynolds, 1997) and affects the aqueous mobility of trace metals. Clay mineralogy also provides information regarding the correlation and origin of Quaternary deposits in the region (Snowden and Priddy, 1968; Autin and others, 1991). Considering that similar Quaternary deposits are present throughout the northern and eastern Mississippi Embayment, the results of this study have implications for Quaternary stratigraphy and protection of ground-water resources in the region.

GEOLOGIC BACKGROUND

Memphis and Shelby County lie in the center of the northern Mississippi Embayment, a trough-shaped basin that plunges southward along an axis that approximates the trace of the Mississippi River. The stratigraphy of the upper Eocene through Holocene sedimentary fill of the Mississippi Embayment in the Memphis area is shown in Table 1 (Graham and Parks,

Table 1. Shallow geologic units underlying Shelby County, Tennessee

System & Series	Group	Stratigraphic unit	Hydro-stratigraphic unit	Thickness	Lithology and hydrologic significance
Quaternary Holocene and Pleis-tocene		Alluvium	(lower part within shal-low aquifer)	0 - 53 m (0 - 175 ft)	Sand, gravel, silt, and clay. Underlies the Mississippi alluvial plain and alluvial plains of tributary streams in western Ten-nessee. Thickest beneath the alluvial plain, where commonly between 100 and 150 feet thick; generally less than 50 feet thick elsewhere. Provides water to domestic, farm, industrial, and irrigation wells in the Mississippi alluvial plain.
Quaternary Pleis-tocene		Loess	(behaves as a leaky con-fining layer is some areas)	O – 20 m (0 - 65 ft)	Silt, silty clay, and minor sand. Principal unit at the surface in upland areas of the Mississippi Embayment. Thickest on the bluffs that border the Mississippi alluvial plain; thinner eastward from the bluffs. Tends to retard downward infiltration of water to the fluvial deposits.
Quater-nary and *Tertiary* Pleis-tocene and Pliocene (?)		Fluvial - terrace deposits	shallow aquifer	0 – 30 m (0-100 ft)	Sand, gravel, minor clay and ferruginous sandstone. Generally underlies the loess in upland areas, but locally absent. Thick-ness varies greatly because of erosional surfaces at top and base. Provides water to many domestic and farm wells in rural areas.
Tertiary Oligocene ? Eocene	?	Jackson Formation and upper part of Clai-borne Group, includes Cockfield and Cook Mountain formations (capping clay)	upper Clai-borne con-fining layer	0 – 114 m (0 – 375 ft)	Clay, silt, sand, and lignite. Because of similarities in lithology, the Jackson For-mation and upper part of the Claiborne Group cannot be reliable subdivided based on available information. Most of the pre-served sequence is the Cockfield and Cook Mountain formations undivided, but locally the Cockfield may be overlain by the Jackson Formation. Serves as the upper confining unit for the Memphis aqui-fer.
	Clai-borne	Memphis Sand ("500-foot" sand)	Memphis aquifer	152 – 271 m (500 – 890 ft)	Sand, clay, and minor lignite. Thick body of sand with lenses of clay at various strati-graphic horizons and minor lignite. Thick-est in the southwestern part of the Memphis area; thinnest in the northeastern part. Principal aquifer providing water for municipal and industrial supplies east of the Mississippi River.

modified from Graham and Parks (1986)

1986). The early to mid-Tertiary-age geologic units beneath Shelby County dip gently to the west and include unconsolidated sand, silt, and clay with minor lignite. Pleistocene and Pliocene(?) fluvial-terrace deposits unconformably overlie the Eocene, mid-Tertiary units. Early workers (Fisk, 1944; Krinitzsky, 1949) identified as many as three terrace levels, based on topography and limited borehole data. More recent studies indicate that as many as four terrace levels are present in valleys of the tributaries to the Mississippi River in Shelby County (Saucier, 1987; Larsen and McClure, 1999; Parks, 1992).

Excluding the present-day tributary valleys, 3 to 20 m of loess overlie the fluvial deposits and mantle the underlying topography. The loess is thickest near the Mississippi River bluff line (Figure 1) (as much as 20 m locally) and thins to the east. Present-day valleys of the Big and Nonconnah creeks, and the Loosahatchie and Wolf rivers contain as much as 18 m of alluvium. The alluvium typically contains sand and gravel near the base and fines upward into sandy and clayey silt. Surface soils in the area are mainly inceptisols and alfisols on the uplands and inceptisols and entisols in the alluvial valleys (Sease and others, 1970).

The geologic units beneath the Memphis and Shelby County area are divided into a series of hydrostratigraphic units, each with its own hydraulic characteristics. The loess and the upper part of the alluvium have similar grain-size and hydraulic properties (Robinson and others, 1997) and behave as leaky, confining units. The loess contains many vertical fractures and root pores that may dominate the hydraulic conductivity (Smith, 1997); thus, the loess may be more conductive than is suggested by its silt-rich grain-size distribution. The fluvial-terrace deposits and the sand and gravel in the lower part of the alluvium comprise the shallow aquifer. Locally, the shallow aquifer includes Mid-Tertiary deposits in areas where sand-rich Eocene or Oligocene deposits directly underlie the fluvial-terrace deposits and alluvium. The shallow aquifer is a water-table aquifer throughout much of the county, but is locally confined by loess along the Mississippi River bluffs and in the Millington area (Parks, 1990; Robinson and others, 1997). The shallow aquifer is used for domestic and farm water supplies in rural parts of Shelby County (Graham and Parks, 1986).

The Cockfield and Cook Mountain formations comprise the lower confining unit for the shallow aquifer and upper confining unit for the Memphis aquifer; this confining unit is termed the upper Claiborne confining unit (Parks, 1990). The total thickness of clay beds in the confining unit varies from less than 3 m to as much as 61 m, suggesting that windows of hydrologic connectivity exist between the underlying Memphis aquifer and overlying shallow aquifer (Parks, 1990). The Memphis aquifer is unconfined in eastern Shelby County, but is generally confined beneath Memphis and throughout western Shelby County. The Memphis aquifer and the correlative Sparta aquifer in northern Mississippi and eastern Arkansas constitute an important agricultural, industrial, and municipal water source for the Mid-South region (Parks and Carmichael, 1990; Hays and others, 1998).

METHODS

Sediment samples were obtained from five wells drilled in association with the USGS National Water-Quality Assessment (NAWQA) program in the Memphis area during 1996. The five wells were chosen from 31 NAWQA wells drilled to obtain samples from differing geomorphic and geographic settings within Shelby County. The Levi and Raleigh sites represent upland settings; the Bartlett and Corsica sites reflect lowland, flood-plain-border areas; and the Halle Park site is in the flood plain of Nonconnah Creek (Figure 1). None of the sites overlies the highest (oldest) fluvial-terrace deposits (McClure, 1999) which may be as old as Pliocene in age (Potter, 1955); thus, the fluvial-terrace deposits sampled in this work are all considered to be Quaternary. Samples were retrieved in two ways: (1) auger drill cuttings, and (2) split spoon samples extracted during drilling from the upper and lower portions of each well. Sampling intervals of 1 to 3 m were used in the upper 10 m, but a 3-m sampling interval was typically used below 10 m. Total drilling depth ranged from 14 to 30 m, depending on the stratigraphic units encountered at individual drilling sites.

Particle size analysis was accomplished using the method of Gee and Bauder (1986) with a pretreatment to remove iron hydroxides and oxides. Precision from triplicate determinations was generally ± 10%. Accuracy, as determined by measurements of prepared standards, was within 3 weight percent of actual values. Organic carbon (OC) contents were determined using the Walkley-Black procedure (Nelson and Sommers, 1982). Precision of triplicate determinations of a sample with low OC content (0.12 weight %) was ± 20%. Cation exchange capacity (CEC) was determined using saturation with a $BaCl_2$ solution followed by displacement by $MgSO_4$ solution (Rhoades, 1982). Precision of

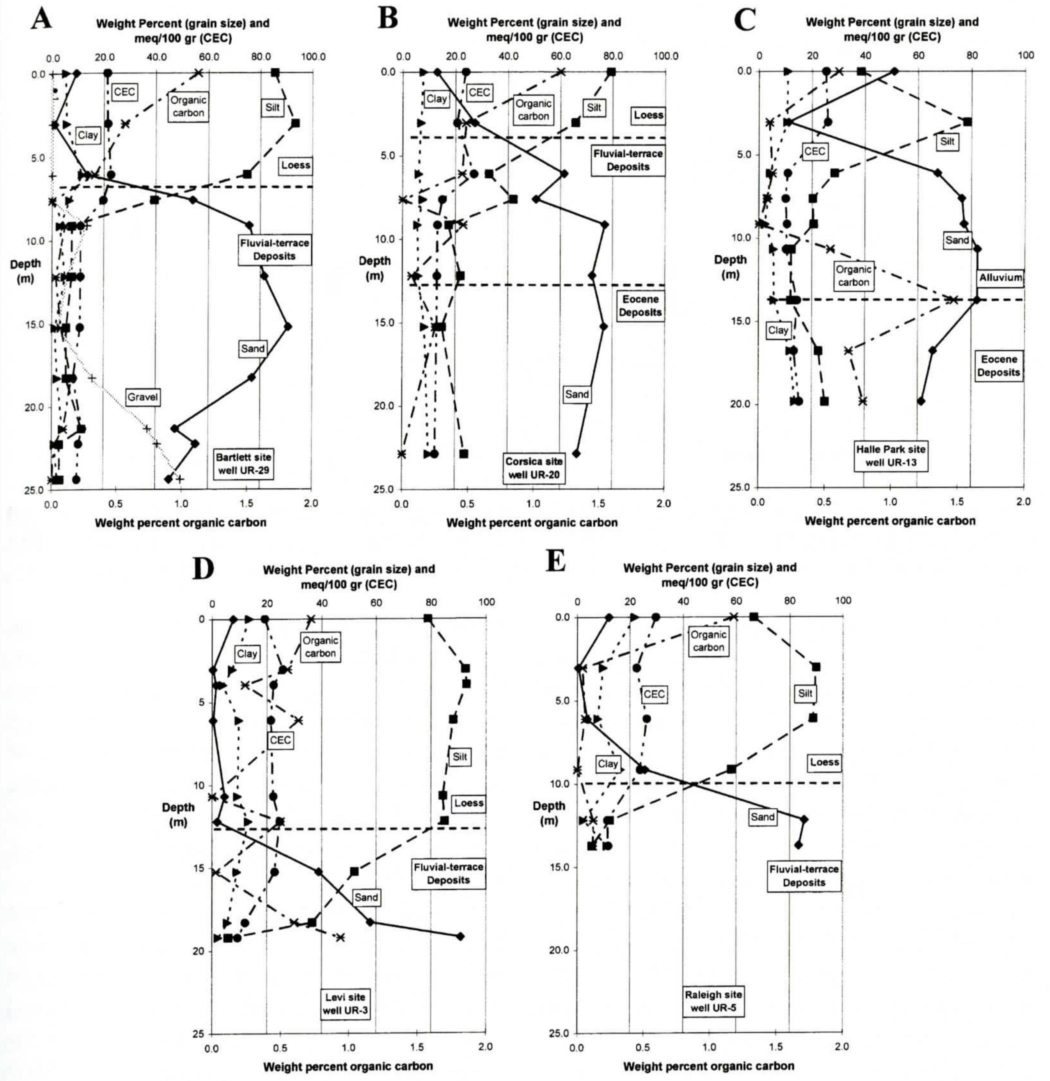

Figure 2. Cross plots of sediment properties versus depth for four of the sample locations. Dashed horizontal lines represent inferred contacts of geologic units.

triplicate determinations of CEC was less than ± 5%.

X-ray diffraction of the clay-size fraction (less than 2 mm) was completed using the Millipore-glass slide preparation method (Moore and Reynolds, 1989). The slides were air-dried and exposed to Cu-Kα radiation from 3 to 35°2q. The presence of smectite was determined by X-ray analysis after solvating in ethylene glycol. The presence of vermiculite was determined by X-ray analysis after solvating in glycerol. Chlorite was discriminated from vermiculite by X-ray analysis following heating of the slides to 300°C for one hour. Semi-quantitative proportions of illite, kaolinite, and smectite were determined using peak area and reference intensity ratios from Moore and Reynolds (1989). The relative abundance of vermiculite and chlorite were assessed qualitatively due to the presence of overlapping peaks.

RESULTS

Four stratigraphic units (loess, alluvium, flu-

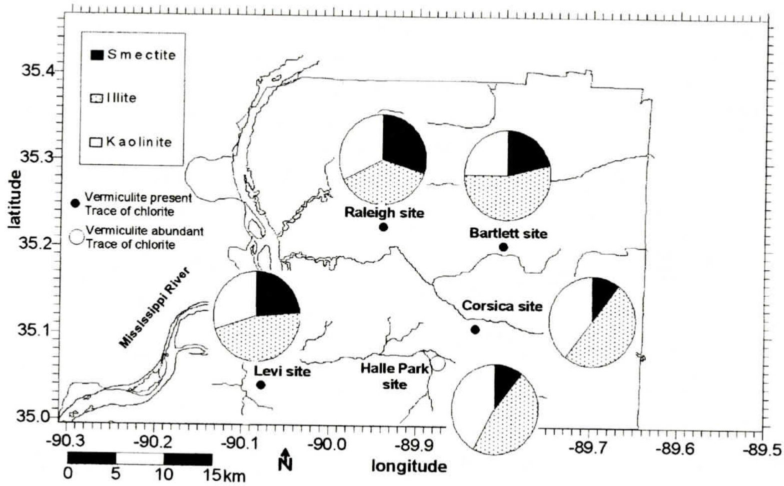

Figure 3. Map of Shelby County with pie diagrams illustrating the average smectite, illite, and kaolinite composition of the alluvium at the Halle Park site and loess at the other four sites. The abundance of chlorite and vermiculite are indicated by the sample location symbol.

vial-terrace deposits, and Eocene deposits) were identified in the five boreholes based upon particle size, color, and correlation to natural gamma response (Strom, 1997). Loess and underlying fluvial-terrace deposits were identified at the Bartlett, Corsica, Levi, and Raleigh drilling sites (data for all sites are shown in Figure 2). In field exposures, a sandy-silt transitional zone (as much as 1.5 m thick) with abundant root traces and mottled colors commonly separates silt-dominated loess from the sand-dominated fluvial-terrace deposits (McClure, 1999). This unit may be reflected in the mixed sand and silt compositions in samples from the drill holes near the loess-fluvial-deposits contact (e.g., 15 to 18 m depth at the Levi site). Alluvium was identified to a depth of 14 m in the Nonconnah Creek flood plain at the Halle Park drilling site (Figure 2). Eocene deposits were encountered beneath the Quaternary deposits at the Corsica and Halle Park sites. The results for the Eocene deposits are presented only for comparison with the Quaternary deposits.

The sediment properties of the loess are fairly homogeneous at the sites investigated. The average grain-size analysis is 85.5% silt, 8.5% clay, and 5.5% sand. Organic carbon contents average 0.3 wt.%, with a range from 0.0 to 1.2 wt.%. The CEC averages 23 meq/100 gr. sediment. The grain-size, OC, and CEC vary little among the four sites (Figure 2), although the Corsica and Bartlett samples are more sandy. The clay mineralogy of the loess is dominated by illite with lesser quantities of kaolinite and smectite (Figure 3). Vermiculite and a trace of chlorite were identified qualitatively in the loess. Surface samples at each site are sandier than the average loess and contain an average of 1.0 wt.% OC.

The sediment properties of the fluvial-terrace deposits are generally more variable than those for the loess, in part reflecting differences in depositional environment and the transitional zone in the upper part of the fluvial-terrace deposits. The average grain-size analysis is 65.0% sand, 20.4% silt, and 5.4% clay. Gravel is present in minor quantities (< 1%) in most cores, but is a major component at the Bartlett site (as much as 49.5% in one sample) (Figure 4). Organic carbon contents average 0.2 wt.%, but range from 0.0 to 0.9 wt.%. The CEC of the fluvial-terrace deposits averages 14 meq/100 gr. sediment, substantially lower than the 23 meq/100 gr. of the loess. The clay mineralogy of the fluvial-terrace deposits is dominated by kaolinite (average of 52%) with lesser quantities of illite (av. of 34%) and smectite (av. of 15%). Chlorite or vermiculite were not identified in the deposits. Aside from the Bartlett site, the average grain size is similar among the other three

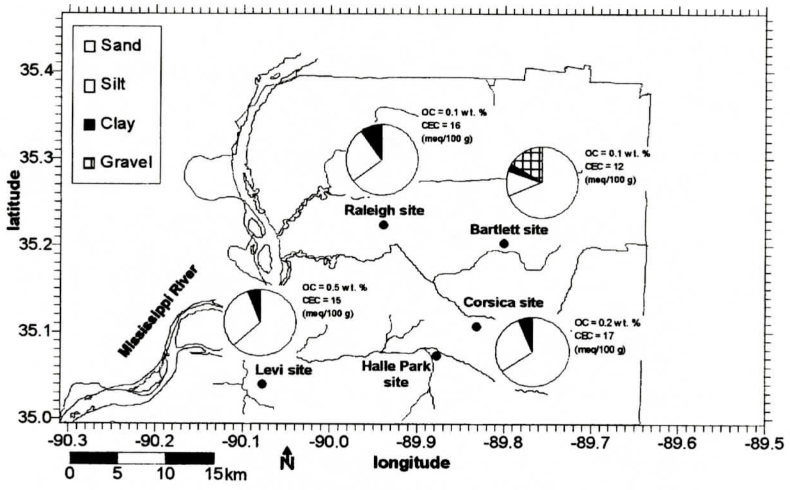

Figure 4. Map of Shelby County with pie diagrams illustrating the average grain size (by weight) of the fluvial-terrace deposits. The average organic carbon (OC) and cation exchange capacity (CEC) of the fluvial-terrace deposits are also indicated for the sample sites.

sites (Figure 4). Organic carbon content appears to correlate with sand content, whereas CEC values increase with increasing silt and clay (Spann, 1997).

The sediment properties of the alluvium are generally intermediate between the loess and fluvial-terrace deposits (Figure 2), with the upper part of the alluvium showing similarity to the loess and the lower part showing similarity to the fluvial-terrace deposits. Similar to the loess sites, the surface sample of the alluvium at Halle Park is more sandy than that at 3 m depth and contains a higher OC content. Grain size in the alluvium generally increases with depth. Gravel is abundant in the lower part of the alluvium in surface exposures throughout the county and in cores from north central Shelby County. The average OC content of the alluvium at Halle Park is 0.4 wt.% with a range of 0.0 to 1.5 wt.%; the highest OC value (1.5 wt.%) is observed at the base of the alluvium. Abundant, coarse-grained wood and seeds are common in the lower part of the alluvium in surface exposures and cores from north-central Shelby County (McClure, 1999; Carmichael and others, 1997). The clay mineralogy clearly reflects contributions from both the loess and fluvial-terrace deposits in the subequal portions of kaolinite, which is the dominant clay mineral in the fluvial-terrace deposits, and illite, which is the dominant clay mineral in the loess (Figures 3 and 5). However, the qualitative abundance of vermiculite is unique to the alluvium. The CEC values are most similar to those in the fluvial-terrace deposits, probably reflecting lower silt content of the alluvium compared to the loess (Spann, 1997).

DISCUSSION

The sediment properties (grain size, OC content, and CEC) for the loess, fluvial-terrace deposits, and alluvium indicate several differences that exist among these units. Analysis of variance (ANOVA) statistical tests of the data indicate that grain size and CEC of the loess are significantly different from those of the other Quaternary deposits at the 95% confidence level (Table 2). The OC contents are not significantly different among the loess, fluvial-terrace deposits, and alluvium, probably because of the wide range of values present in each unit. The grain size and CEC of the fluvial-terrace deposits and the alluvium are not significantly different from each other at the 95% confidence level, based on ANOVA testing (Table 2). However, this may be a result of how these units were defined during this study. As defined in this study, the fluvial-terrace deposits and the alluvium contain significant intervals of

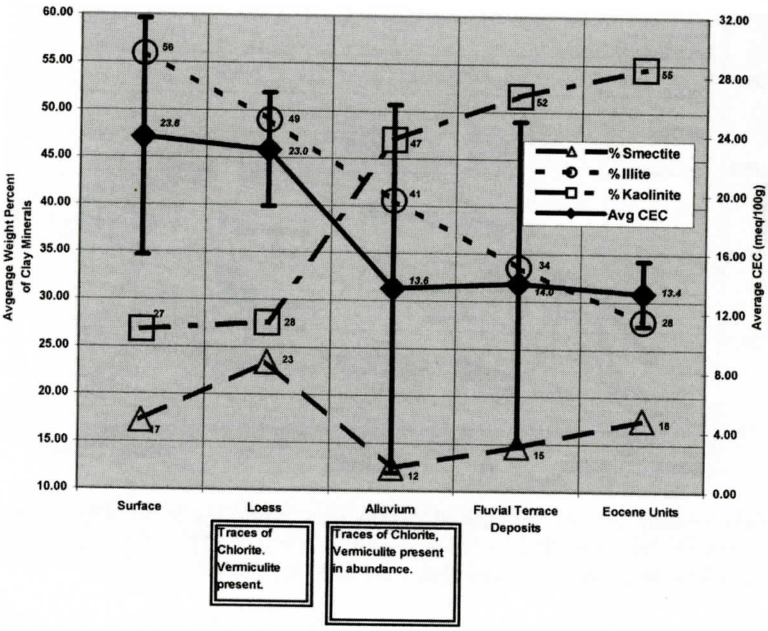

Figure 5. Plot of average smectite, illite, and kaolinite proportions in the clay mineral fraction and average CEC values for the surface soil, loess, alluvium, fluvial-terrace deposits, and Eocene units. Qualitative presence of chlorite and vermiculite are also indicated.

silty material; in the fluvial-terrace deposits as a transitional zone beneath the loess and in the alluvium as the reworked loess in the upper part of the alluvium.

Some of the sediment properties vary according to geomorphic position in the landscape. Except for the sand content, all other properties of the loess from the individual sites are not statistically different at the 95% confidence level (Table 3). Increased sand contents are observed in the two sites (Corsica and Bartlett) that border tributary streams. This may reflect accumulation of sandy silt sheet-wash or flood deposits along the borders of the tributary flood plains at these sites. Alternatively, sand may in part have been incorporated into the loess samples during the drilling process. For the fluvial deposits, all properties, except the gravel content, from the individual sites are not significantly different at the 95% confidence level (Table 3). Gravel contents vary across the county, but seem to be consistently greater along tributary stream channels (McClure, 1999), such as Fletcher Creek near the Bartlett drill site. Organic carbon contents are lower in the topographically higher fluvial-terrace locations (Raleigh and Bartlett). This may reflect the older age of these deposits compared to the topographically lower Levi and Corsica sites.

The clay mineralogy influences the CEC values for the various units. In general, the average CEC value is inversely related to kaolinite abundance (Figure 5). This is expected because smectite, illite, and vermiculite each typically have higher CEC values than kaolinite (Langmuir, 1997). Within the alluvium the CEC is highly correlated (r = 0.93) with illite abundance (and presumably vermiculite) and anti-correlated (r = - 0.81) with kaolinite abundance in individual samples. Relationships between CEC and mineralogy are not present within the loess or fluvial-terrace deposits. The absence of such correlation in the loess is probably due to the homogeneity in the clay mineralogy of the loess; however, the same argument does not hold true for the fluvial-terrace deposits.

The clay mineralogy of the Quaternary units varies systematically and provides insight toward correlation and understanding the origin of the loess, alluvium, and fluvial-terrace de-

Table 2. ANOVA test results (á= 5%) comparing properties among stratigraphic units

	Sand	Silt	Clay	Organic Carbon Content	Cation Exchange Capacity
Critical F Value	4.2252	4.2252	4.2252	4.2252	4.2252
Loess & Fluvial Deposits	85.7214	112.0020	4.7919	4.2226	24.8277
Critical F Value	4.6001	4.6001	4.6001	4.6001	4.6001
Loess & Alluvium	43.3146	44.0337	4.7433	0.0286	20.3340
Critical F Value	4.3009	4.3009	4.3009	4.3009	4.3009
Fluvial Deposits & Alluvium	0.0115	0.7655	0.0037	1.8952	0.0201

Note: Gray shades indicate tests which failed.

posits. The clay mineralogy of the fluvial-terrace deposits is dominated by kaolinite and illite with lesser quantities of smectite, all of which are present in similar percentages in sediments of the underlying Eocene Claiborne Group (Figure 5) (Jeffers, 1982; Hertzing, 1984; White, 1985). A similar dominance of kaolinite is recorded by Snowden and Priddy (1968) for pre-loess gravels that they correlated to "Citronelle Formation" in southern Mississippi. Paleosols on the Upland Complex gravel deposits in the lower Mississippi Valley (Autin and others, 1991) show a similar dominance of kaolinite. Presumably, these clay minerals were eroded from Eocene Claiborne Group and Pliocene(?)-Pleistocene fluvial deposits sediments during Quaternary incision of the western Tennessee and northern Mississippi landscape and deposited along with sand and gravel. However, weathering in soil environments, such as those represented by Upland Complex paleosols, undoubtedly contributed to the kaolinite dominance. Much of the gravel in the Quaternary units in Shelby County appears to be reworked from older (Pliocene(?)-Pleistocene) gravels (McClure, 1999) associated with an ancestral mid-continental drainage system (Potter, 1955; Self, 1993).

The clay mineralogy of the loess in Shelby County is comparable, although more illitic, to loess in Mississippi (Snowden and Priddy, 1968) and eastern Arkansas (Markewich, 1994). The similarity in clay mineralogy of loess across the region and difference from that of the underlying strata is attributed to the source of the loess. Mixing of sediments in the Mississippi River valley followed by erosion of silt and dispersal by eolian processes (Autin and others, 1991) led to a homogenous clay mineral composition in the loess. The clay mineral composition of the loess was modified in-situ by weathering processes as indicated by common vermiculite in surface soils and weathered loess deposits. Vermiculite is well known to form in Holocene and late Pleistocene soils (Douglas, 1977; Righi and Meunier, 1995), but is virtually absent in older strata. The clay mineralogy of the alluvium is interpreted to represent a mixture of clays from the loess and fluvial-terrace deposits, although direct contributions from the Eocene Claiborne Group may also be important locally. The abundance of vermiculite in the alluvium is thought to reflect the importance of eroded loess-rich surface soil in the sediment composition of the alluvium.

The sediment properties have implications for potential contaminant migration through Quaternary sediments in the eastern Mississippi Embayment. In either upland or flood-plain areas, the velocity of aqueous contaminants introduced near the surface will be retarded as they pass through a silty deposit, either loess, reworked loess of the upper alluvium, or the transitional upper part of the fluvial-terrace deposits. These deposits contain the highest CEC and OC values determined in this study. The CEC values are consistently high among these fine-grained units (approximately 25 meq/100gr). The OC values are highly variable. In the loess, high OC values may reflect buried soils within the sequence. In the upper alluvium at Halle Park relatively low OC values were observed, although coarse-grained organic fragments (logs, branches, etc.) are commonly observed in stream cut-bank exposures of the upper alluvium throughout Shelby County.

Table 3. ANOVA test results (á= 5%) comparing properties within the loess

	Sand	Silt	Clay	Organic Carbon Content	
Critical F Value	4.7571	4.7571	4.7571	4.7571	
ANOVA - Loess	11.5823	3.9724	0.0816	1.5138	
	Cation Exchange Capacity	% Smectite	% Illite	% Kaolinite	
Critical F Value	4.7571	4.7571	4.7571	4.7571	
ANOVA - Loess	1.0683	0.8718	3.9920	0.2484	
	Sand	Silt	Clay	Gravel	
Critical F Value	3.3439	3.3439	3.3439	3.3439	
ANOVA - Fluvial Deposits	0.0184	1.6945	3.1928	3.4349	
	Organic Carbon Content	Cation Exchange Capacity	% Smectite	% Illite	% Kaolinite
Critical F Value	3.3439	3.3439	3.3439	3.3439	3.3439
ANOVA - Fluvial Deposits	2.8858	1.0289	2.518	5.6581	6.4310

However, widely distributed coarse-grained organic material may be of limited aid in retarding migration of organic compounds. Furthermore, large root pores present throughout the loess (Smith, 1997) and upper alluvium may allow waters bearing contaminants to infiltrate readily and limit opportunities for cation exchange or sorption. The fluvial-terrace deposits and lower part of the alluvium generally contain the lowest CEC and OC values, although the highest OC occurred at the base of the alluvium and is probably associated with coarse-grained organic fragments. The lower parts of the fluvial-terrace deposits and alluvium have the highest permeability of the Quaternary units (Robinson and others, 1997; Broshears and Bradley, 1991), and the least potential for contaminant retardation. Once contaminants are present in the lower alluvium and fluvial-terrace deposits, only limited retardation is expected along hydrologic flow paths.

CONCLUSIONS

Sediment properties determined in samples of Quaternary deposits in Shelby County, Tennessee, vary among the three stratigraphic units, fluvial-terrace deposits, loess, and alluvium. The loess is generally homogeneous and has the highest CEC and OC values. The fluvial-terrace deposits have variable sediment property values and the lowest CEC and OC values. The alluvium also has variable sediment property values, with the lower alluvium generally similar to the fluvial-terrace deposits and the upper alluvium similar to the loess.

The clay mineral compositions of the loess and fluvial-terrace deposits are distinctly different. The clay mineralogy of the loess reflects the homogeneous composition of eolian silt, presumably eroded from flood plains in the Mississippi River valley, and minor modifications due to soil-forming processes. The kaolinite-rich clay mineralogy of the fluvial-terrace deposits is likely derived largely from that of the Eocene Claiborne Group, although weathering may have also been important. The clay mineral composition of the alluvium reflects a mixture of the fluvial-terrace and loess sources, but also shows more indication of weathering.

The CEC and OC values of the Quaternary deposits, in concert with hydrologic information, suggest that contaminant migration may be retarded during matrix infiltration through the loess and upper alluvium. The potential for contaminant migration in the fluvial-terrace deposits and lower alluvium is much greater owing to lower CEC and OC values and higher hydraulic conductivity in these units.

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EOCENE BASALT VOLCANISM IN CENTRAL VIRGINIA: IMPLICATIONS FOR CENOZOIC TECTONISM

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ABSTRACT

Recent geomorphological and structural studies indicate that the North American margin has undergone regional uplift since the Cenozoic. Eocene volcanics from Virginia, the youngest igneous rocks in the eastern United States, are spatially and temporally correlated with this uplift. Their location is in close proximity to two earlier eruptive sequences, the Precambrian Catoctin basalts and the Mesozoic Appalachian tholeiites (MAT). The geochemical signatures of these basalt suites help constrain evolution of eastern North America. Primitive Eocene basalts contain 8-12 wt.% MgO, 235-630 ppm Cr and up to 160 ppm Ni, so they provide insight into the geochemical and thermal structure of the mantle source region in Cenozoic time. The Eocene basalts are geochemically distinct from both the Catoctin lavas and the MAT, requiring derivation from different source regions. The Eocene and Catoctin lavas have higher incompatible trace element abundances and lower initial Sr-isotope values than the MAT, but lack the anomalous relative depletions in Nb and TiO_2 that are observed in the Mesozoic suite. The apparent depth of melting is greatest for the Eocene lavas (ca. 50-70 km), and the lack of an arc-like signature suggests melting occurred at depths greater than the lithospheric source region of the MAT. The cause of Cenozoic basalt magmatism and regional uplift is not known, and may result from far-field stresses associated with convergence of the North American and Caribbean Plates or from small-scale convection along the craton edge as reflected also by development of the Bermuda Rise.

INTRODUCTION

The eastern portion of North America has undergone repeated tectonic modification since the Grenville orogeny ~1 Ga. These tectonic events are preserved, in part, in mafic lavas that date from the opening of Iapetus at 570 Ma and the formation of the Atlantic Ocean. An Eocene basalt sequence exposed in central Appalachian Valley of Virginia is spatially collocated with these two earlier suites, but is not associated with a known tectonic episode. By comparing the geochemistry of the Eocene basalts with that of the Precambrian Catoctin flood basalts and the Mesozoic Appalachian tholeiites, we document that the long-term evolution of the eastern North American craton has involved substantial geochemical modification and, potentially, removal of extensive portions of the subcontinental lithosphere.

Eocene magmatism is temporally associated with Cenozoic uplift of the Appalachian margin as manifest in extensive exposures of coastal plain sediments and the uplift of the Blue Ridge front. This uplift is reflected also in the lack of correspondence between the Atlantic-Gulf of Mexico drainage divide and the modern topographic expression of the Appalachian Mountains. The driving mechanism of the uplift is not

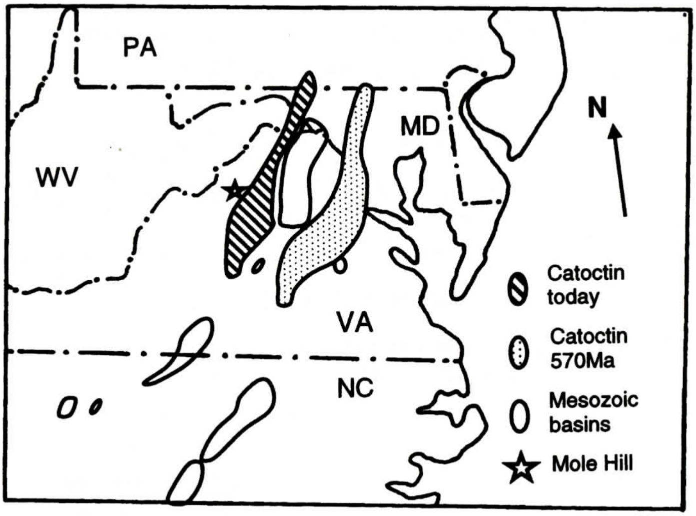

Figure 1. Modern physiography and distribution of the mafic lavas reported in this study. The shaded region encompasses known Cenozoic dikes and lavas, and the stippled field reflects reconstructed position of the Catoctin province during Mesozoic rifting (after Badger and Sinha, 1988).

known, but it is likely related to the thermal event that triggered Eocene volcanism. Our new geochemical data suggest involvement of a sublithospheric source region which in turn requires thermal and material flux from deep within the mantle.

GEOLOGIC SETTING AND MAGMATIC HISTORY

The central Appalachian region was deformed during Proterozoic and Paleozoic orogenies and subsequently extended during formation of the Atlantic Ocean. Some of these tectonic events left a magmatic record, enabling us to assess long-term changes to the underlying lithosphere. The Precambrian Blue Ridge Basement Complex (Sinha and Bartholomew, 1984) is uncomformably overlain by basalts of the Catoctin Formation that record magmatism associated with rifting during formation of Iapetus (e.g., Rankin, 1975). The Catoctin Formation comprises subaerial and submarine basalts, including local pillow lavas, and has been dated at 570 Ma (Badger and Sinha, 1988). The regional extent of the Catoctin Formation has been estimated at over 11,000 km^2 (Badger, 1989), making it the largest flood basalt province in eastern North America.

The Blue Ridge region sustained pervasive low-grade metamorphism of probable Taconic age (Mose and Nagel, 1984; Pettingill and others, 1984), followed by an inferred Carboniferous subduction event along the southeastern portion of the margin (Sinha and Zeitz, 1982). Granitic magmatic activity associated with this event was followed by extensive west-vergent thrusting during the Alleghenian orogeny. Modern geomorphic features generally date from this last event, although there is evidence for Cenozoic modification of the topographic front and associated drainage divides (Clark and Knapp, 2001).

Two sets of Mesozoic dikes cut the Appalachian structures: the first are tholeiitic diabases associated with rifting ~195-200 Ma (Pegram, 1990), and the second are somewhat younger alkalic rocks of variable composition (Johnson and others, 1971; Southworth and others, 1993). The Mesozoic Appalachian tholeiites (MAT) are confined to the eastern flank of the Blue Ridge, where they are commonly associated with Triassic sedimentary basins (Weigand and Ragland, 1970; Pegram, 1990). The alkalic intrusions in western Virginia and West Virginia comprise kimberlites, nepheline syenites and more saturated units including andesites and picrites (Johnson and others, 1971; Southworth and others, 1993). The majority of these rocks have not been dated, but available data cluster around 150 Ma (Southworth and others, 1993).

The youngest igneous activity in the region occurred west of the Blue Ridge (figure 1), and has been termed the Shenandoah igneous province (McHone, 1988). This magmatic event dated at about 43-48 Ma (Fullagar and Bottino, 1969; Southworth and others, 1993) produced mildly alkalic rocks including basalts, lamprophyres and trachytes, that form the focus of the present study.

MOLE HILL BASALT

Petrography

The easternmost Eocene unit is Mole Hill, an olivine-spinel basalt plug dated at 48±1 Ma (Wampler and Dooley, 1975). It was emplaced into Ordovician carbonates, although the contacts are not exposed. The unit shows local crude columnar jointing and most samples are quite fresh.

The Mole Hill basalt is uniformly fine-grained, with less than 10 vol.% phenocrysts and xenocrysts of olivine, plagioclase feldspar, clinopyroxene and spinel (Johnson and others, 1971). The groundmass is primarily plagioclase feldspar with minor olivine and pyroxene. One-atmosphere melting experiments found olivine on the liquidus between 1190°–1200°C, followed by plagioclase feldspar (1182°–1190°C) and augite (1170°–1164°C) (Bartels and Furman, 2002). Petrographic observations match this sequence, suggesting minor crystallization occurred after emplacement. Olivine and clinopyroxene phenocryst compositions ($Fo_{76\text{-}90}$, $En_{\sim 87}$; Dudas and others, in preparation) also suggest low-pressure fractionation.

Mole Hill contains xenoliths (<5 cm) of olivine-bearing clinopyroxenite, as well as sparse country rock inclusions (Johnson and others, 1971). Olivine and pyroxene xenocryst compositions are more magnesian than the phenocrysts, and the high alumina contents of the pyroxenes are consistent with a moderate-pres-

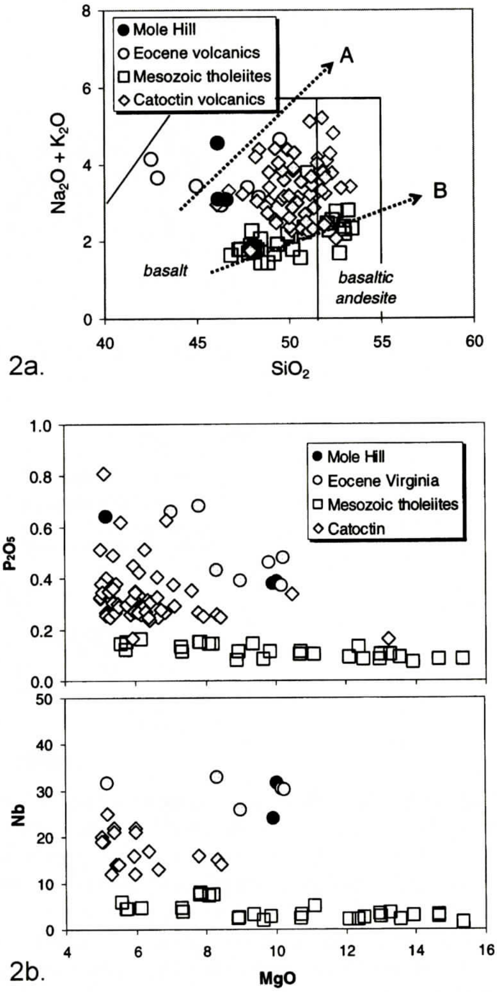

Figure 2. (A) Total alkalis – silica variations in Eocene mafic volcanics (trend A) indicate these lavas are undersaturated with respect to silica relative to both the Catoctin (Badger, 1989) and the Mesozoic Appalachian tholeiite (trend B; Pegram, 1990) suites.
(B) Whole-rock geochemical characteristics. Eocene mafic lavas have higher abundances of incompatible major (P_2O_5) and trace (Nb) elements – for a given MgO content – than samples from the Catoctin and Mesozoic Appalachian tholeiite groups.

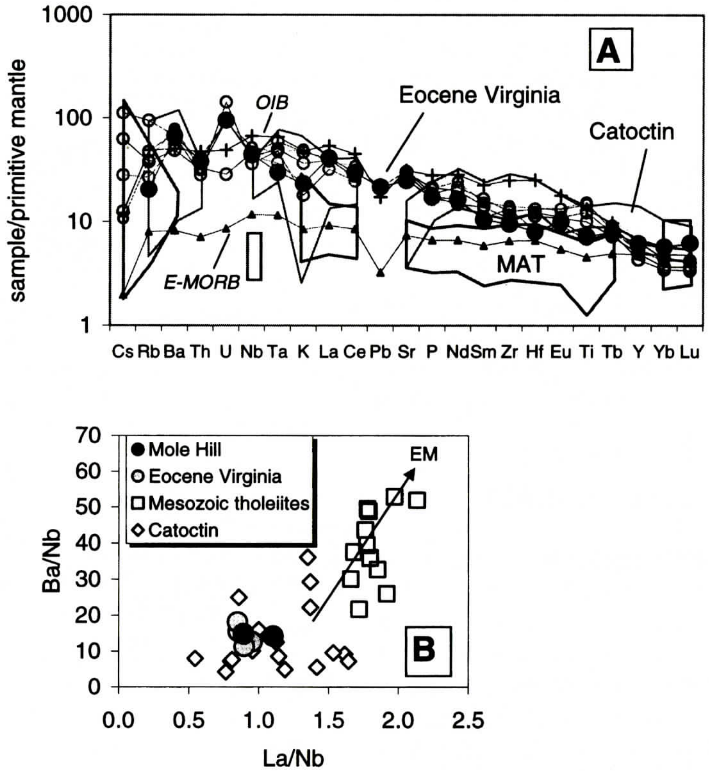

Figure 3. (A) Primitive mantle-normalized incompatible trace element distributions of Eocene basalts, Mesozoic Appalachian tholeiites (MAT) and Catoctin volcanics (normalizing values of Sun and McDonough, 1989). The Catoctin and Eocene series have abundances similar to those of ocean island basalts (OIB) whereas the MAT abundances are lower, within the range of E-MORB, and display marked negative anomalies for Nb and Ti. Sources of data as in figure 2. (B) La/Nb-Ba/Nb observed among Eocene basalts fall in the range of ocean island basalts, while Catoctin and MAT data extend to higher values and define a trend towards enriched mantle (EM) compositions.

sure origin. The phase compositions and mineral textures suggest that the clinopyroxenites represent fragments of the uppermost mantle, perhaps the source region for the Mole Hill magma (Dudas and others, in preparation).

Samples analyzed in this study come from Mole Hill (VAH-1; FD1) and from an Ordovician limestone quarry in northern Highland County, VA (VAH-2, VAH-3). The latter two samples are from narrow (<30 cm) trachytic and basaltic dikes where contamination by country rock is likely to have occurred.

Major and Trace Element Geochemistry

The Mole Hill basalt is mildly nepheline normative ($\leq$10%), and its bulk composition is typical of the Shenandoah Eocene mafic lavas (Southworth and others, 1993; figure 2). Major element trends within the Eocene series are consistent with the low-pressure experimental results (Bartels and Furman, 2002) indicating progressive removal of olivine and plagioclase feldspar, joined by clinopyroxene at roughly 8 wt.% MgO. Mole Hill samples with 8-12 wt.% MgO have abundances of compatible trace elements ($\leq$160 ppm Ni, 235-630 ppm Cr, 30-38 ppm Sc; table 1) that indicate they have not un-

Table 1. Bulk Geochemical Analyses

Sample	VAH-1	VAH-2	VAH-3
SiO_2	45.66	68.74	42.06
TiO_2	1.59	0.29	3.39
Al_2O_3	15.43	15.25	14.96
Fe_2O_3	11.71	3.44	14.61
MgO	9.92	0.64	7.96
MnO	0.21	0.19	0.21
CaO	11.98	1.78	11.90
Na_2O	2.36	5.08	2.60
K_2O	0.70	3.39	1.50
P_2O_5	0.38	0.13	0.46
Total	99.94	98.93	99.65
Cs	bdl		0.3
Rb	13	50	25
Ba	471	1447	556
Sr	527	496	647
Th	3.2	7.0	2.7
U	2	3	2
Pb	4	7	4
Nb	31.7	58.5	37.2
Ta	1.2		1.9
Zr	106	584	159
Hf	2.5		4.2
Y	28	22	24
Sc	32.5		30.0
V	236	1	141
Cr	286	1	17
Co	56.3		50.0
Ni	159	bdl	14
La	28.3	55.3	25.9
Ce	53.2	94.6	61.3
Nd	22.3		33.1
Sm	4.6		6.8
Eu	1.7		2.3
Tb	0.9		0.9
Yb	2.8		2.1
Lu	0.5		0.3

Major and selected trace elements analyzed by XRF at the University of Massachusetts (Amherst); Cs, Ta, Sc, Co and REE analyzed by INAA at the Massachusetts Institute of Technology. Precision based on replicate analyses is <1% for most major elements; <2% for MnO, K_2O, P_2O_5, Ba, Sr, Cr, Y, Zr, Nb, LREE and MREE; <5% for U, Pb, Ta, Th, Hf, V, Ni, Sc, Cs, Rb and HREE.

dergone substantial fractionation since separating from the mantle source region. This interpretation is consistent with the paucity of observed phenocrysts.

Individual incompatible trace elements are poorly correlated within the Eocene basalt series (figure 2). This observation may reflect the small compositional range of the Eocene lavas, or may indicate heterogeneous conditions of melting and emplacement of the individual eruptive units. Chondrite-normalized REE patterns of the Eocene basalts are generally parallel to one another; they lack Eu anomalies and have moderate negative slopes (La/Yb_n 6.7-10.1). Abundances of incompatible trace elements normalized to primitive mantle values are higher than those observed in MORB, but are similar to abundances measured in ocean island basalts (Sun and McDonough, 1989; figure 3a). Values of La/Nb and Ba/Nb (Figure 3b) and Sr/Ce (~10) are within expected ranges for primitive mantle-derived lavas. In contrast, values of Nb/U (16-19) and Ce/Pb (13-15) are lower than those observed in primitive mantle-derived mafic lavas and thus suggest a more complicated genetic history.

Radiogenic Isotope Geochemistry

Sr isotope compositions of the Eocene volcanic rocks range from 0.70319 in a clinopyroxene xenocryst from Mole Hill to 0.70454 in the trachyte (table 2). Analyses of two different Mole Hill basalts range from 0.70348-0.70353, varying only slightly beyond analytical error. Values of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ are strongly correlated among these samples (figure 4a). The Mole Hill basalt samples and the Eocene trachyte have overlapping $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ values; the Mole Hill clinopyroxene xenocryst has Pb isotope values that differ only slightly from those of the host basalt (figure 4b). Basalt VAH-3 has unusually high Pb isotope ratios (table 2), consistent with contamination by host limestone.

Table 2. Isotopic data.

Sample	Location	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
VAH-1	Mole Hill	0.703482	0.512821	19.436	15.620	39.079
FD1	Mole Hill	0.703528	0.512787	19.412	15.640	39.089
FD1 cpx	Mole Hill	0.703185	0.512848	19.142	15.674	38.880
VAH-3	Highland Co.	0.703433	0.512913	20.210	15.699	39.448
VAH-2	Highland Co.	0.704538	0.512740	19.317	15.621	39.056

All analyses were carried out at the Massachusetts Institute of Technology; F. Dudas (analyst).

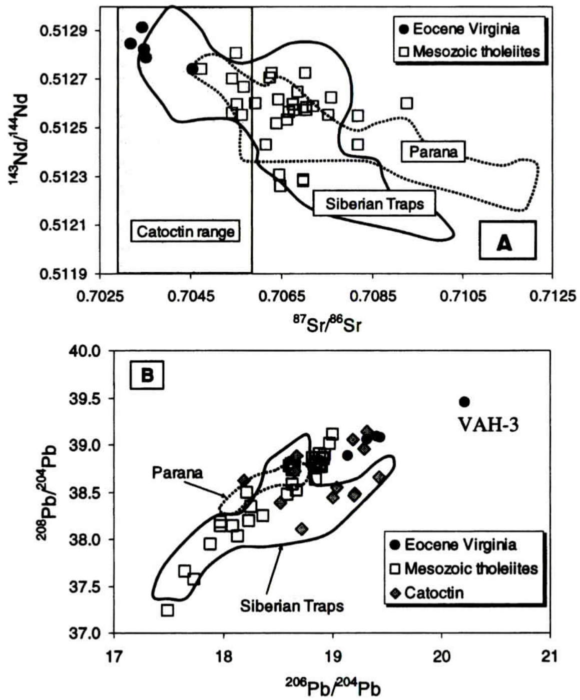

Figure 4. (A) Sr-Nd isotope values of the Eocene basalts are consistently less radiogenic than those of the MAT, and overlap endmember values observed for continental flood basalts (data from Sharma and others, 1992; Hawkesworth and others, 1993; Arndt and others, 1998; Gibson and others, 1999). Trachyte VAH-2 has a higher Sr-isotope value. The Catoctin basalts have not been analyzed for Nd isotopes, but their Sr isotope data overlap the Eocene basalts and extend to more radiogenic values.
(B) Pb-Pb isotope values of the Eocene basalts overlap selected Catoctin lavas and are slightly more radiogenic than the MAT and other continental flood basalt sequences. Dike sample VAH-3 has unusually radiogenic Pb isotope values, consistent with contamination by host limestone.

Comparison to Catoctin Flood Basalts and Mesozoic Appalachian Tholeiites

The Eocene basalts are more highly undersaturated with respect to silica than either the Catoctin lavas or the MAT (figure 2a). It is worth noting that Catoctin basalts are restricted to compositions with less than ~8 wt.% MgO, while the Eocene and MAT series include more primitive samples with up to 10 and 11 wt.% MgO, respectively.

The Eocene mafic samples have consistently higher concentrations of incompatible major

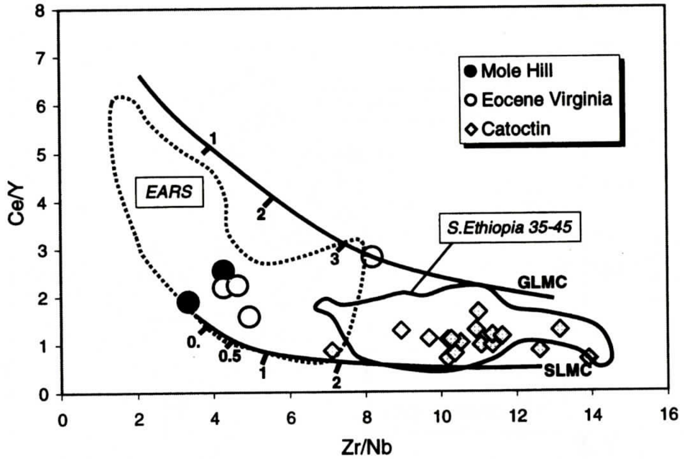

Figure 5. Zr/Nb-Ce/Y variations in mafic lavas. The solid lines are non-modal fractional melting curves calculated by Hardarson & Fitton (1991) for spinel lherzolite (SLMC) and garnet lherzolite (GLMC). Numbers on these lines refer to melt percentages. Data from the Eocene lavas plot at pressures between the SLMC and GLMC, falling within the range of mafic lavas from highly extended portions of the East African Rift System (EARS; Macdonald and others, 2001; Furman and others, in press). Catoctin volcanics plot at higher degrees of melting than the Eocene lavas, and overlap the range of lithosphere-derived Tertiary mafic lavas from southern Ethiopia (George and Rogers, 2002; Furman and others, in press). MAT samples lack Y data and are therefore not plotted; their Zr/Nb values range from 12-20. Sources of data as in Figure 2.

(TiO_2, P_2O_5) and most trace (e.g., La, Sr, Ba, Nb but not Zr, Hf) elements than the MAT and Catoctin basalts at comparable MgO contents (figure 2b). The most distinctive geochemical feature of the MAT – negative anomalies for Nb and Ti – is not observed in the Eocene or Catoctin basalts (figure 3a). The HFSE depletions of the MAT were described in detail by Pegram (1990), who concluded they represent an inherited feature of the MAT source region, consistent with its modification by arc accretion during an orogenic event.

The Eocene and Catoctin suites have overlapping ranges of Ba/Rb, Rb/Sr and Zr/Hf values but distinct Zr/Nb-Ce/Y (figure 5) variations that preclude their derivation by melting a common, homogeneous source composition. Although the Catoctin lavas have undergone pervasive low-degree metamorphism, it is unlikely that refractory high field strength (HFSE) and rare earth elements (REE) were significantly mobilized (e.g., Badger and Sinha, 1988). Variations among these elements therefore likely reflect conditions of melting and emplacement of the individual suites, and may have implications for their genesis as discussed below.

Sr isotope values measured in the Eocene suite fall within the range observed for the Catoctin basalts (Badger and Sinha, 1988; Badger, 1989), but are distinctly less radiogenic than values measured for the MAT (Pegram, 1990) and other continental flood basalts (figure 4a). Values of $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ measured at Mole Hill overlap the most highly radiogenic Catoctin basalts (Badger and Sinha, 1988; Badger, 1989), but extend to higher $^{206}Pb/^{204}Pb$ than the MAT suite (Pegram, 1990; figure 4b). None of the Eocene rock samples have the distinctive high $^{207}Pb/^{204}Pb$ values observed in the MAT (Pegram, 1990), although the clinopyroxene xenocryst plots within the MAT range.

DISCUSSION

The spatial coincidence of three suites of mafic volcanic rocks – the Eocene volcanic series, the Mesozoic Appalachian tholeiites and the Cambrian Catoctin flood basalts – makes it pos-

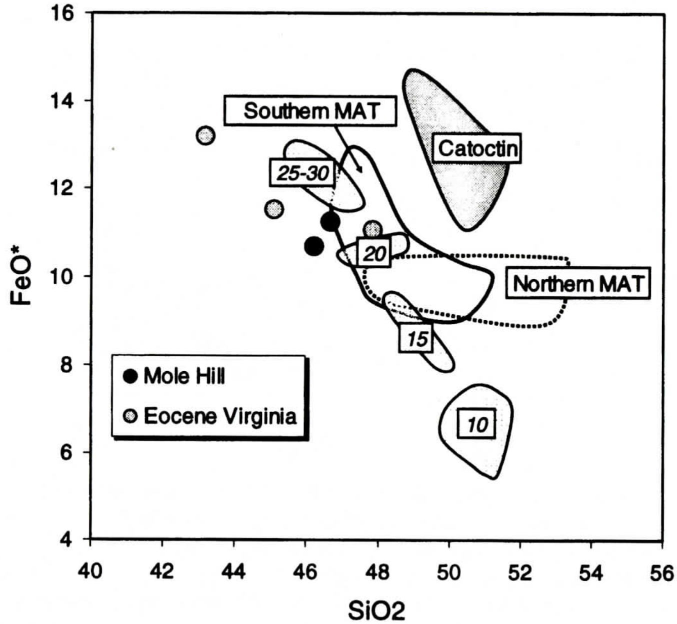

Figure 6. FeO^* versus SiO_2 for selected mafic suites and experimental melts in equilibrium with fertile mantle peridotite (Hirose & Kushiro, 1993; Baker & Stolper, 1994). Major element compositions were renormalized with total iron as FeO, then corrected for olivine fractionation to correspond to experimentally derived melts of fertile peridotite (Mg# ~72); only samples with Mg# >62 were corrected using this procedure. Experimental data are plotted as reported, and are shown in the shaded fields. Eocene lavas overlap the range of experimental melts from fertile peridotite at ≥20 kbar. The Catoctin basalts define a similar range of FeO^* at higher SiO_2 contents, while compositions of the MAT are consistent with melting at comparable or lower pressures. Pressures estimated on the basis of this diagram are approximate, as isobaric experiments are not directly analogous to natural systems generated by adiabatic decompression melting; however, the relative pressures inferred for EARS suites are useful for comparative purposes. The position of individual samples on this diagram can be affected by the melt percentage, as melting past the removal of clinopyroxene results in higher values of both SiO_2 and FeO^* (Wasylenki *et al.*, 2003). The position of the Eocene samples adjacent to the experimental fields suggests melt segregation from a clinopyroxene-bearing source, whereas the high SiO_2 contents of Catoctin lavas and the northern MAT indicate clinopyroxene was consumed during melting. Sources of data as in figure 2.

sible to explore the evolution of the lithospheric and/or sublithospheric source regions underlying eastern North America for a period of over 500 million years. The geochemistry of these mafic rocks provides insight into the mineralogy of the source region and the depths and degrees of melting associated with each magmatic episode. These parameters in turn help constrain the thermal history of the continental margin during repeated tectonic events.

Conditions of Mantle Melting

Abundances of FeO^* and SiO_2 in primitive Eocene volcanics (back-corrected for olivine fractionation) overlap the experimentally determined fields for melts of fertile peridotite at pressures greater than 20 kbar (Hirose and Kushiro, 1993; Baker and Stolper, 1994; figure 6). The Catoctin lavas have consistently higher FeO^* and SiO_2 contents than the Eocene basalts, suggesting melting continued beyond consumption of clinopyroxene in the Catoctin suite, whereas melting likely occurred in the presence of clinopyroxene in the case of the Eocene lavas (Wasylenki and others, 2003). Two interpretations are possible: (1) Eocene lavas were generated by smaller degrees of melting at pressures in the same range as those under which the Catoctin basalts were formed, or (2) the source region for Eocene lavas was richer in clinopyroxene than that from which the Catoctin lavas were derived.

The SiO_2 and FeO* contents of all northern and many southern Mesozoic Appalachian tholeiites suggest the MAT were also derived by melting at somewhat lower depths and greater extents than the Eocene basalts. The normative nepheline contents of the Eocene volcanics support this qualitative scheme, requiring melting at greater depths than those inferred for the hypersthene- and quartz-normative MAT and Catoctin lavas.

Further support for this interpretation comes from Zr/Nb-Ce/Y variations in Eocene and Catoctin mafic lavas (figure 5). All Eocene samples fall within the range of asthenosphere-derived lavas from the East African Rift (Macdonald and others, 2001; Furman and others, in press), falling between melting curves calculated for spinel- and garnet-peridotite source regions at low degrees of melting (Hardarson and Fitton, 1991). In contrast, Catoctin and MAT samples have much higher Zr/Nb values that plot within the range of lithosphere-derived melts representing shallower depths and greater extents of melting (George and Rogers, 2002; Furman and others in press).

Finally, chondrite-normalized Tb/Yb values of the Eocene mafic lavas (1.8-2.5) are much higher than those of the MAT (0.6-1.2), suggesting the Eocene lavas were derived by melting in the stability field of garnet or a clinopyroxene with high Ca-Tschermak's component (Blundy and others, 1998). Regardless of the specific pressure involved, it is clear that the Eocene lavas reflect a lower extent of melting at pressures greater than those of the other mafic suites.

Composition of the Source Regions

Reconstruction of the late Paleozoic continental margin suggests that the Catoctin lavas erupted from a source region eastward of their present outcrop location, within the area corresponding to the Mesozoic rift basins and basalt sequences. During Eocene time, this same region became the source area for renewed basalt magmatism. The geochemical features of these three suites, however, require distinct mantle sources that, in turn, indicate a complex thermal and tectonic history.

The Catoctin volcanics reflect incipient opening of the Iapetus Ocean (Rankin, 1975). Their bulk rock geochemistry and initial Sr-isotope values suggest they were derived by melting depleted upper mantle material, followed by substantial removal of olivine and subordinate plagioclase feldspar and clinopyroxene (Badger and Sinha, 1988). This process would generate a large gabbro body at the base of the crust, consistent with the observed positive gravity anomaly that parallels the modern Appalachians.

The distinctive arc-like trace element features of the Mesozoic Appalachian tholeiites clearly require a different source region beneath this portion of the craton. Primitive Mesozoic tholeiites, like other continental flood basalt suites, have more highly radiogenic isotopic signatures (figure 4) indicative of melting an enriched mantle lithosphere (e.g., Pegram, 1990). The MAT likely record the addition of a slab component to the North American lithosphere (Pegram, 1990). The emplacement of this arc must post-date eruption of the Catoctin volcanics, and is likely Carboniferous as proposed by Sinha and Zeitz (1982) on the basis of plutonic occurrences in the southern Appalachian region.

In the Eocene, however, there is no evidence for arc-like geochemical signatures. Instead, the Eocene lavas record low degrees of melting from a deeper mantle source with less-radiogenic lithophile isotope ratios, similar to those found in ocean island basalts. The isotopic composition of the Eocene basalts ($^{87}Sr/^{86}Sr$ ~0.7035, $^{143}Nd/^{144}Nd$ ~0.5128, $^{206}Pb/^{204}Pb$ ~19.4, $^{208}Pb/^{204}Pb$ ~39.0) falls within the range of deep mantle values known as FOZO (Hart and others, 1982) or C (Hanan and Graham, 1996). This component is recognized as contributing to magmatism in the ocean basins, both along mid-ocean ridges and at hot spots. While some Catoctin lavas also sample this common composition, it is not observed in the MAT. The incompatible trace element abundances of Eocene mafic lavas are also consistent with melting of a sub-lithospheric source region. For example, values of K/Nb and K/La (normalized to primitive mantle abundances; Sun and McDonough, 1989) in the Eocene suite are typically less than unity, indicating the source region lacks amphibole. In contrast, K/Nb and K/La values in the MAT are consistently greater than unity, suggesting a lithospheric source with hydrous phase(s).

Taken together, the geochemical evidence indicates that the Eocene source region is located within the asthenosphere rather than the subcontinental lithosphere. This suggestion has significant implications for the thermal evolution of the North American margin.

Neotectonics of the Appalachian Margin

Broad topographic uplift and arching along major thrust faults like the Pen Branch in central South Carolina are now known to be coeval with the Eocene emergence of the upper Coastal Plain (Bartholomew and others, 2002). Extension above the buried portion of this fault is apparently associated with small normal faults and a series of clastic dikes, all oriented parallel to the dominant regional joint set. In addition, syndepositional folding and faulting, as well as many unconformities of varying extent, have been mapped in the upper Coastal Plain of Georgia and South Carolina (Bartholomew and others, 2002). Together, these features document significant seismic – presumably tectonic – events during late Eocene time. There is no evidence for widespread Eocene igneous activity as would be predicted from upwelling asthenosphere beneath the southeastern North American coastal margin. However, several lines of evidence suggest that the Cenozoic tectonic evolution of this region involved thermally-induced tectonic uplift that is preserved today in, for example, onshore exposures of late Cretaceous through Tertiary strata of the Atlantic Basin from New Jersey southward to the Yucatan Peninsula (Colquhoun and others, 1991; Knapp, 2001). Regional topographic anomalies such as the Blue Ridge escarpment and the lack of correspondence between the eastern US drainage divide and the Appalachian topography suggest that the North American margin has been affected by tectonism in Cenozoic time (Hack, 1982; Clark and Knapp, 2001).

No attempt has been made to correlate Eocene structures in central Virginia with those exposed in the southeastern Coastal Plain. It is interesting to note that the drainage divides of the Jackson River and the South Branch Potomac River are located along a 100-km structural high that overlaps the most abundant Eocene activity (Southworth and others, 1993), suggesting a relationship between topography and magmatic activity that is not apparent further south. The Eocene volcanics are emplaced along fractures that are locally indistinguishable in orientation from the dominant Jurassic dike set, although a general lack of age constraints precludes making a definitive assessment. Individual Eocene dikes may trend either northwest or northeast, suggesting either a complex stress field during emplacement or the utilization of extant planes of weakness by the ascending basalts (Southworth and others, 1993).

Bartholomew and others (2002) conclude that far-field tectonic activity related to the convergence of the North American and Caribbean plates played an important role in shaping the structural and magmatic character of the southeastern North American margin. Progressive counter-clockwise rotation of North American relative to the Caribbean plate documented in the middle Eocene (Donnelly, 1989) is consistent with the observed rotation of the stress field in South Carolina and Georgia. Alternatively, Manspeizer and others, (1989) and Vogt (1991) note that the middle Eocene Shenandoah igneous province is temporally correlative with the formation of the Bermuda Rise (45-33 Ma; Jaroslow and Tucholke, 1994), suggesting a possible relationship between these igneous features. The Eocene volcanics, as well as the uplifted southern Appalachians and the Cape Fear arch, lie within landward projections of the Bermuda Rise, leaving open the possibility that they formed through a common process. One possibility, first proposed by Vogt (1991) and later described in detail by King and Ritsema (2000), is that small-scale convective cells within the upper mantle may develop along the edges of stable continental cratonal areas. The geochemistry of the Eocene basalts – in particular their isotopic affinity to the deep mantle source region – is consistent with this model, providing support for a scenario of thermally-driven Cenozoic tectonic uplift along the North American coastal plain.

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